Universidade de Aveiro Departamento de Engenharia Mecânica
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FAUSTO TUCCI

Modelação e simulação numérica de processos de pultrusão

Modelling and numerical simulation of pultrusion processes

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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Engenharia Mecânica, realizada sob a orientação científica do Doutor Robertt A. F. Valente, Professor Auxiliar do Departamento de Engenharia Mecânica da Universidade de Aveiro, Portugal, e co-orientação científica do Doutor Pierpaolo Carlone, Professor Auxiliar do Departamento de Engenharia Industrial da Universidade de Salerno, Itália.

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palavras-chave

Pultrusão; Método dos Elementos Finitos; Modelos termo-químicos com acoplamento mecânico; ABAQUS; subrotinas de utilizador.

resumo

O objectivo deste trabalho prende-se com a modelação e análise por simulação numérica, através do Método dos Elementos Finitos, da distribuição de temperaturas (e sua evolução) durante reações de polimerização das resinas em compósitos sujeitos a processos de pultrusão. A modelação baseou-se numa abordagem quasi-estática num enquadramento tridimensional e a partir de pressupostos de base Eulerianos para as equações de evolução. A um modelo inicial termo-químico foi acoplado um modelo mecânico de equilíbrio, por forma a estimar por meio de simulação numérica o perfil das tensões decorrentes do processo de conformação, bem como as deformações associadas. A implementação do modelo numérico por elementos finitos foi realizada através da utilização do programa comercial ABAQUS, por meio do desenvolvimento de uma série de subrotinas de utilizador (em linguagem Fortran) desenvolvidas pelo autor deste trabalho.

keywords

Pultrusion; Finite Element Method; Thermo-chemical-mechanical models; ABAQUS; User subroutines.

abstract

The focus of this work is the implementation of a Finite Element model for the simulation of temperature distributions and evolutions during the exothermic reaction of polymerization of resins in pultrusion processes. The problem has been modelled using a quasi-static approach in a three-dimensional Eulerian domain. To the thermochemical model it was sequentially coupled the resolution of typical mechanical balance equations, in order to numerically estimate the stress levels within the material and the corresponding strains. The implementation of the numerical finite element model was carried out using the ABAQUS finite element software, by means of a number of user subroutines (in Fortran language) implemented by the author.

Summary

List of figures

List of symbols

V_m	Matrix volumetric fraction
V_f	Fiber volumetric fraction
M_m	Matrix mass fraction
M_f	Fiber mass fraction
ρ	Mass density
ε	Strain
σ	Stress
E	Young modulus
ν	Poisson ratio
G	Shear modulus
τ	Tangential tension
$\underline{\underline{S}}$	Flexibility matrix
$\underline{\underline{T}}$	Rotation matrix
$\underline{\underline{Q}}$	Lamina's constitutive matrix
$\underline{K}$	Laminate's mid-plane curvature
μ	Viscosity
E_a	Energy of activation
R	Universal gas constant
T	Temperature
α	Degree of cure
Q	Macroscopic flow
K	Permeability
S_P	Area of the passage section
L	Length of the fluid path
ΔP	Pressure gradient
C_p	Specific heat at constant pressure
t	Time
u	Profile speed
$K_{L,c}$	Longitudinal composite thermal conductivities
$K_{T,c}$	Transversal composite thermal conductivities
K_d	Die thermal conductivities
q	Heat generation
H_{tr}	Total heat amount produced during the complete reaction
$R_r(\alpha, T)$	Rate of resin reaction
E_0	Totally uncured resin Young modulus
E_∞	Totally cured resin Young modulus
T_{c1}	Critical temperature of starting of the glass transition
T_{c2}	Critical temperature of ending of the glass transition
T_g	Instantaneous glass transition temperature
T_{g0}	Instantaneous glass transition temperature of the uncured resin
k_f	Fiber isotropic bulk modulus
k_r	Resin isotropic bulk modulus

k_t	Effective plane strain bulk modulus
$\underline{\underline{J}}$	Jacobian matrix
CTE	Coefficient of thermal expansion
ΔV_r	Incremental specific volume shrinkage of the resin
V_{sh}	Total volumetric shrinkage
h_i	Spatial increment

1. Introduction

Pultrusion is one of the processes that in recent years are attracting the attention of academics and researchers due to the involved materials, mechanical properties of the products and for process economic aspect. It is a production process of long-fiber constant cross-sectional composite profiles with thermosetting resin matrix. By means of pultrusion processes it is possible to make products with a very high volume ratio of fiber, of any length value. Usually the products have a high surface quality and do not require further finishing operations. The process is simple and highly automatable, where the high efficiency in conversion of raw materials further promotes its convenience.

However the pultrusion process involves a wide range of technological problems related to the complex fluid-dynamic, thermal, chemical and mechanical phenomena involved in the process. Whereby it is necessary to carry out real and virtual experiments to cope with all the physical problems that then turn into defects or weaknesses of the product or process.

This work aims to simulate and analyse some of the phenomena that take place in the dies, during pultrusion, and which strongly influence the characteristics of the finished product. In particular it is proposed to describe the thermo-chemical and mechanical fields.

The thermochemical field is influenced by the fact that the mold is subjected to the action of the heating plates and that the polymerization process, triggered by the high temperature set, is strongly exothermic whereby the composite (in particular the resin present in the composite) becomes a heat source. For this reason, thermal and chemical problems are coupled and cannot be solved separately.

The mechanical field variables are, on the other hand, influenced by several factors. The most influential is the polymerization of the composite resin that transforms from a liquid-solid mixture in the finished product required. It is clear that the change of state of aggregation of the resin affects the mechanical characteristics of the profile. Another determining factor in the mechanical behaviour is the interaction between the walls of the mold and the profile that, again, depends on the degree of cure of the resin present in the composite. They were also taken into account in this work the thermal expansion of fiber and matrix and the chemical resin shrinkage, the degree of cure.

The present work has the purpose of calculate in each point of the composite profile the values of temperature, degree of cure, stress and strain. It has been used for this purpose the ABAQUS computational suite, for the analysis of the physics of the system, using the Finite Element Method as the most suitable tool. Within this context, a number of user subroutines in Fortran language were implemented for the modelling and computation of all the phenomena and interactions involved.

In the following chapters, a summary description of composite materials is provided, including their structure and the advantages and disadvantages arising from their use. Also analyses and both micromechanical and macromechanical aspect of the lamina are provided, with a brief insight into the classical laminates theory. Subsequently, it follows a classification of the most frequently used materials for the production of composite with an attempt to accurately describe

the impregnation and polymerization phenomena together with the mechanical interaction between fibers and matrices. Finally, it is listed and briefly described the most common composite manufacturing processes available.
In the third chapter, the pultrusion process and all its components are described in more detail. The materials commonly used and the related technological problems are listed. The advantages and disadvantages are analysed and main applications have been described.
The focus of the fourth chapter is the numerical analysis work. It is reported a brief introduction to numerical methods and the role they have in engineering. Finite Element Method and ABAQUS software, used for the analyses are also briefly described. After this point, there is the description of the whole program developed in ABAQUS environment and all subroutines built for the analysis of the phenomena.
The fifth chapter contains the conclusions and discussions about the obtained results, where also potential ideas are given for the continuation of this work, together with possible works developable in the future.

2. Composite materials

2.1 Introduction

This work deals with the numerical simulation of the pultrusion process, using the Finite Element Method. In summary, pultrusion is a process of producing composite materials with a constant cross section.

Composite materials have been increasingly used since the Second World War because of the resistance and lightness that they can guarantee. The growing demand for high performance materials, initially associated to military applications in the aeronautical field, led since the 40s to the development of materials that can exceed the mechanical properties of metals and their alloys, but at the same time with a more favorable weight / strength ratio.

The combination of two or more different materials in a composite part produces structures that have widespread application. In fact, nowadays the use of composite materials has spread to many fields, mainly in those areas of production where it is necessary to meet the needs of low weight and high mechanical characteristics (aeronautical / aerospace, sports, medicine). This is linked to the progressive improvement of systems production, which has led to a greater flexibility of use that allows to satisfy a considerable range of demands.

Particularly in the aerospace sector, the need to optimize the operational performance of structures is imperative, mainly because of the costs of putting components into orbit, and is based on the careful selection of materials and design to avoid oversized solutions and ensure no weaknesses . In the case of satellites and unmanned space probes, the weight of the structure represents only 7-8% of their total weight at launch. Therefore to get great resistance combined with extreme lightness, are widely used parts made with thicknesses of a few tenths of a millimetre. Given the growing aeronautics dissemination, advanced composite materials were also quickly introduced in the terrestrial and marine transport to fulfil the same needs for higher performance with lower consumption. The racing industry has been obviously what more quickly understood the importance of novelty and in 1981 the first frame for a Formula1 single-seater was made. The advantages of a carbon-fiber body were not just related to the overall lightness, but also to higher torsional rigidity, compared to that of the corresponding aluminium frames. It was possible then to get a better alignment and a better effectiveness of the car. In the nautical field, as in the automobile, competitions started introducing composites in boat building. Already in 1979, the US boat Eclipse, winner of the Admiral's Cup, presented hull and deck made of composite glass and aramid fiber mixture. Today racing boats, whose class rules allow the use of these materials, have the hull, deck, trees, sheets, ropes and other small details of construction products with high strength fibers.

In the commercial sector of recreational boating the use of composites has rapidly expanded. In this field, in addition to mechanical properties, it is essential an high resistance to corrosion, that composites have compared to metallic alloys. Also their absolute nonmagnetic characteristic makes them suitable for the top coating of structures used at military boats.

Even in the sports sector the diffusion of the composite materials was very sudden and embraced a large amount of disciplines in which the lightness of the gears used, allowed the athletes to do less effort and get better results. Within the products achieved, tennis rackets with carbon fiber reinforcements, ski, river downhill canoe, fishing rods, golf and hockey clubs, bows and arrows, spears and rods for the jump, frames and wheels for bicycles, bob and many other items are examples including advanced composite materials. With regard to the industrial plant engineering, composite materials are already being used for purposes which are very dissimilar to each other, such as, tanks coatings for gas or liquids under pressure, air conditioning conductors, cryogenic conduits, reinforcement windings for flexible rubber tubes, hydro-pneumatic pipes, high-pressure pipes.

The aramid fibers are used as a resistant element of transmission belts and toothed, of conveyor belts resistant to corrosion, and are becoming increasingly popular in the construction of mooring ropes and cables, in which they can provide resistance level equal to steel ropes, lower elongation and lightness similar to synthetic ropes with longer life. An additional feature of aramid fibers is the big impact resistance, namely the ability to absorb large dynamic stresses without major damage. The industries specializing in ballistic protection, therefore, have immediately adopted the use of these materials for the production of bulletproof vests, armour plates and screens.

Recently, orthopaedic medicine has begun using advanced composite materials in the construction of replacements of parts of the human body. In particular, carbon fibers, aramid fibers and glass fibers are employed in the construction of load-bearing structures of the prosthesis, especially those of the lower limbs. The diversity of characteristics among the various fibers (such as the rigidity for the carbon and the elasticity for aramid fibers), and the possibility to make products with differentiated stratification, allow to develop structures characterized by variable deformability which can reproduce the characteristics of human bone. Because of the great resistance and lightness, combined with excellent tolerability by the body, composite materials are preferred to stainless steel, titanium-vanadium compounds and aluminium alloys, which are only retained for the joints where the composite solutions would be penalized by increased wear conditions [5],[8],[10].

2.2 Composite material structure

Composite materials are a three-dimensional combination of at least two immiscible elements. Because of that their structure is non homogeneous. The components are each other in contact and they are separated by a clear interface. Each component has a specific set of chemical-physical properties, both in a macroscopic and in a structural view. Since the mix is not homogeneous, the resulting material has characteristics different from the individual constituents. The most commonly used composite materials are usually composed of several layers, in which a fibrous reinforcement (with the purpose of supporting the loads) embedded in a matrix. This matrix has no tasks of mechanical strength, but transmits the load to the fibers and ensure the chemical resistance and the cohesion between the fibers of a same layer and between adjacent layers. The fibers actually act as reinforcement because the mechanical properties of a material increases with decreasing sample size. This is because of the less probability of presence of imperfections and since the production processes of the fibers reduce the surface defects. Due to these features, the composite have quite different behaviour compared to the common materials which are homogeneous and isotropic (Fig 1).

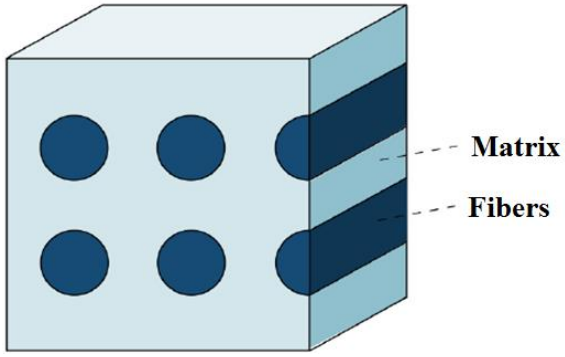

Fig 1: Long unidirectional fibers composite structure, [8]

There are different kind of composite material in relation to the fiber type used [5]:

- **Long fibers composite:** the fibers are arranged along a direction in which higher mechanical strength is desired (Fig 2a). In fact, if it's desired mechanical strength in more than one direction it is possible to use different layers with fiber disposed in different orientation or it is possible to use fiber fabrics in which fibers are disposed along more than one direction (Fig 2b). Since the fibers have a specific orientation this kind of composite are anisotropic.
- **Short fibers composite:** the fibers are very short with respect to the size of the composite and are disposed in a random way. In this case the fibers are just a filler who give a better mechanical behaviour to the matrix. The mechanical performance of the short fibers composite are not as good as the long fibers composite (when the load is in the fiber direction), but this kind of composite material can be assumed (in a macroscopic view) to be isotropic.

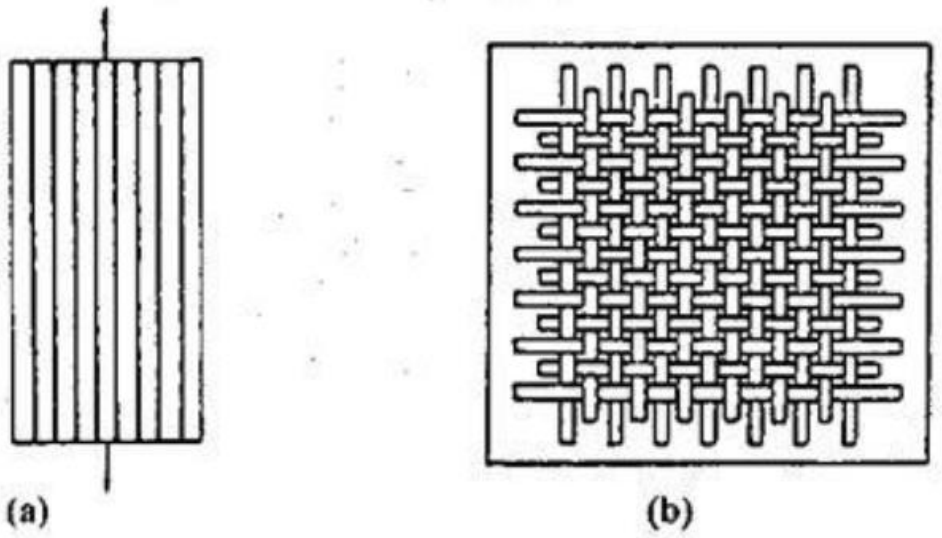

Fig 2: Long fibers composite

- **Mat fibers composite:** the reinforcement is composed of a fabric of randomly disposed long fibers. This kind of composite is macroscopically isotropic and it has mechanical features usually better than the short fiber composite.
- **Particle composite:** the reinforcement is made of ceramic or metallic particle mixed in the matrix. This is the less expensive kind of composite material and hence the most widely used. It's possible to define two different categories of particle composite: (a) large particle composites, which act by restraining the movement of the matrix, and (b) dispersion-strengthened composites, containing 10-100 nm particles, in which the matrix bears the major portion of the applied load and the small particles hinder dislocation motion, limiting plastic deformation. Usually the particle composites are macroscopically isotropic.

The composite materials presents several advantages in confront of the classical materials and alloys. The first one (and probably the most important) advantage are the very highs ratios strength to weight and stiffness to weight. Also the fatigue properties are generally better than the metals. Composite materials also have a good resistance to corrosion. There are many automated manufacturing process that makes low the production cost and the scraps [5].

There are also some disadvantages linked to composite materials. So far it is difficult to design it because of the lack of a unified theory on the polymerization of the resins, the models of which are almost always of experimental nature [10]. The composite materials have bad behaviour when they are subjected to concentrated loads. There are also problem with disposal and recycling them [5].

2.3 Micromechanical and macromechanical behaviour

In order to describe the mechanical properties of a long fiber composite material, in this work it is taken into account a single layer composed of unidirectional parallel fibers. This kind of layer, because of its composition, results orthotropic, and in particular transversally isotropic. The mechanical performances required to the material come from the microscopic interaction between fibers and matrix. This analysis is based on the hypothesis of perfect adhesion between fibers and matrix, and on the hypothesis of small deformation (contained in the elastic field of both the component) [5].

❖ **Micromechanical analysis**

Taking into account a single layer of composite, it is possible to define four important quantities:

- Matrix volumetric fraction, defined as the ratio between the matrix volume and the total composite volume: $V_m = {Matrix\ volume}/{Total\ composit\ volume}$
- Fiber volumetric fraction, defined as the ratio between the fiber volume and the total composite volume: $V_f = {Fiber\ volume}/{Total\ composit\ volume}$
- Matrix mass fraction, defined as the ratio between the matrix mass and the total composite volume: $M_m = {Matrix\ mass}/{Total\ composit\ mass}$
- Fiber mass fraction, defined as the ratio between the fiber volume and the total composite volume: $M_f = {Fiber\ mass}/{Total\ composit\ mass}$

It results that: $V_m + V_f = 1$ and $M_m + M_f = 1$. Volumetric and mass factor are linked to each other by means of the density:

$$M_i = \frac{m_i}{m_c} = \frac{\rho_i v_i}{\rho_c v_c} = \frac{\rho_i}{\rho_c} V_i \quad , \quad i = m, f \tag{1}$$

In this formulation, m_f and m_m are respectively the mass of the fibers and of the matrix, and v_f and v_m are the volume of the fibers and of the matrix. The subscript "c" refers to the lumped composite. It is possible describe the properties of the composite in function of those quantities. The lumped composite density can be computed in the following way:

$$\rho_c = \frac{m_f + m_m}{v_c} = \rho_f V_f + \rho_m V_m \tag{2}$$

In the following it is considered a composite layer subjected to a force directed as the fibers (Fig3). This is the most common and most desirable situation because the loads are directed as the most resistant direction of the composite, being considered true the iso-deformation hypothesis. It means that the fibers, the matrix and the lumped composite are subject to the same deformation $\varepsilon_f = \varepsilon_m = \varepsilon_c$. In this case it is easy to compute the Young modulus in the longitudinal direction by means the modulus of the component which results in the relation (3).

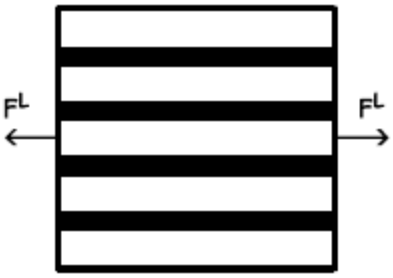

Fig 3: Representation of a longitudinal load

$$E^L = V_m E_m + V_f E_f \tag{3}$$

It is also important to compute the strength in the less desirable situation, in which the loads are orthogonal to the fiber direction, as shown in (Fig 4). In this situation it is considered the hypothesis of iso-stress that means that the fibers, the matrix and the lumped composite are subject to the same stress $\sigma_f = \sigma_m = \sigma_c$.

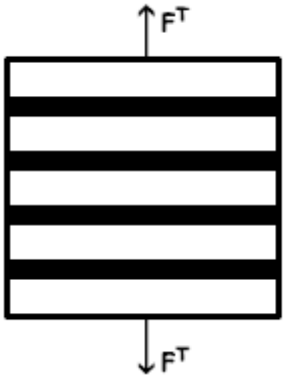

Fig 4: Representation of a transversal load

In this case is possible to compute the Young modulus in the transversal direction by means the following equation:

$$\frac{1}{E^T} = \frac{V_f}{E_f} + \frac{V_m}{E_m} \tag{4}$$

It is also possible define a Poison ratio of the lumped layer as: $\nu^{LT} = -\frac{\varepsilon^T}{\varepsilon^L}$.

From this relation it results the equation:

$$\nu^{LT} = \nu^f V_f + \nu^m V_m \tag{5}$$

The last relevant value necessary for the characterization of the composite is the tangential elastic modulus computed in the frame of reference and defined by the fibers direction and the transversal one (Fig 5). In the hypothesis that both fibers and matrix are subjected to the same tangential stress, it results in the following relation:

$$\frac{1}{G^{LT}} = \frac{V_m}{G_m} + \frac{V_f}{G_f} \tag{6}$$

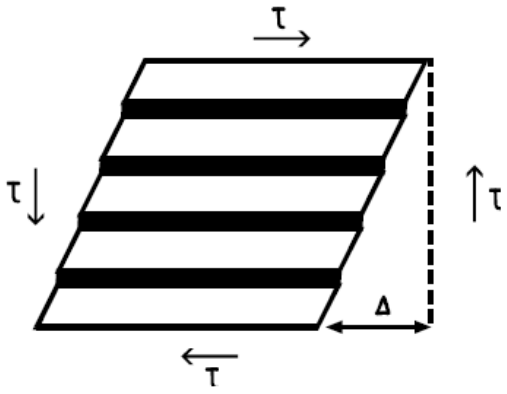

Fig 5: Representation of a shear load

❖ Macromechanical analysis

With the values $E^L, E^T, \nu^{LT}, G^{LT}$ it is possible to define the behaviour of the lumped composite by means its constitutive equation. In the hypothesis of small (elastic) deformation the constitutive equation is $\underline{\varepsilon} = \underline{\underline{S}}\,\underline{\sigma}$, in which $\underline{\varepsilon}$ is a vector [6X1] containing the six terms of the deformation, $\underline{\sigma}$ is a vector [6X1] containing the six terms of the stress and $\underline{\underline{S}}$ is the flexibility matrix [6X6]. Taking into account a single layer, it is possible to approximate the problem by means of the plane stress hypothesis if the loads in the thickness direction are negligible. In this case the vectors are:

$$\underline{\varepsilon}^{LT} = \begin{bmatrix} \varepsilon^L \\ \varepsilon^T \\ \gamma^{LT} \end{bmatrix} \;;\; \underline{\sigma}^{LT} = \begin{bmatrix} \sigma^L \\ \sigma^T \\ \tau^{LT} \end{bmatrix}, \tag{7}$$

in which ε^L and ε^T are the deformation, respectively, in longitudinal direction and in transversal direction, γ^{LT} is the distortion in the plane L-T, σ^L and σ^T are the normal tension respectively in longitudinal direction and in transversal direction, τ^{LT} is the tangential tension in the plane L-T. It then results in the flexibility matrix:

$$\underline{\underline{S^{LT}}} = \begin{bmatrix} \frac{1}{E^L} & -\frac{\nu^{TL}}{E^T} & 0 \\ -\frac{\nu^{LT}}{E^T} & \frac{1}{E^T} & 0 \\ 0 & 0 & \frac{1}{G^{LT}} \end{bmatrix} \tag{8}$$

It is possible to make this equation more general by extending it to all the planar frame of reference by means of a rotation matrix. For a frame of reference *x-y* rotated of an angle α with respect to the frame of reference L-T it is possible to write the following relation:

$$\underline{\sigma}^{LT} = \begin{bmatrix} cos^2\alpha & sin^2\alpha & -2\sin\alpha\cos\alpha \\ sin^2\alpha & cos^2\alpha & 2\sin\alpha\cos\alpha \\ \sin\alpha\cos\alpha & -\sin\alpha\cos\alpha & cos^2\alpha - sin^2\alpha \end{bmatrix} * \begin{bmatrix} \sigma^x \\ \sigma^y \\ \tau^{xy} \end{bmatrix} = \underline{\underline{T}} * \underline{\sigma}^{xy} \tag{8}$$

$$\begin{bmatrix} \varepsilon^L \\ \varepsilon^T \\ \gamma^{LT}/_2 \end{bmatrix} = \underline{\underline{T}} * \begin{bmatrix} \varepsilon^x \\ \varepsilon^y \\ \gamma^{xy}/_2 \end{bmatrix} \; ; \; \underline{\underline{J}} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1/_2 \end{bmatrix} \Longrightarrow \underline{\varepsilon}^{LT} = \underline{\underline{J}}^{-1} * \underline{\underline{T}} * \underline{\underline{J}} * \underline{\varepsilon}^{xy} \tag{9}$$

So it is possible to find out the relation between the stress and the strain in a generic frame of reference *x*-*y*:

$$\underline{\sigma}^{LT} = \underline{\underline{\underline{\underline{S}}}}^{LT} * \underline{\varepsilon}^{LT} \Rightarrow \underline{\sigma}^{xy} = \underline{\underline{T}}^{-1} \underline{\underline{\underline{\underline{S}}}}^{LT} * \underline{\underline{J}}^{-1} * \underline{\underline{T}} * \underline{\underline{J}} * \underline{\varepsilon}^{xy} \;\; , \tag{10}$$

which results in the generic constitutive equation for a layer of long fiber composite:

$$\underline{\sigma}^{xy} = \underline{\underline{Q}} * \underline{\varepsilon}^{xy} \tag{11}$$

The constitutive equation of the lamina written in this compact form (11) is very useful, as described in the next chapter, for the constitutive equation of the laminate construction.

2.4 Laminate theory

The focus of laminate theory is to describe the mechanical properties of laminates composite materials. The laminates are one of the most interesting application of the long fibers composite materials. A laminate is an organized sequence of unidirectional reinforced layers, called laminas (Fig 6). Each lamina is disposed with the fibers in different orientations in order to overcome the anisotropy problem. Since it is impossible to choose a main reference simultaneously for all the layers, it is fixed a generic system x-y-z, placing the axes so as to keep the x-y plane on the middle plane of the laminate [6].

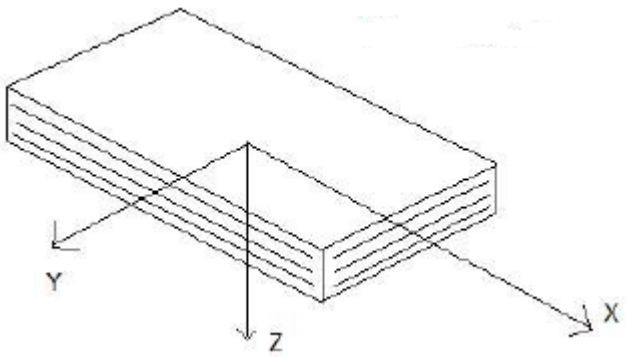

Fig 6: Representation of a laminate, [6]

Each one layers is uniquely defined by fiber orientation.
The laminate theory is based on the following assumptions [6]:

- the strains are small enough to avoid plasticity;
- each lamina is considered to be a homogeneous layer;
- no slip is allowed between the adjacent layers which means that the displacement components are continuous through the thickness;
- each lamina is assume to follow a state of plane stress;
- The laminate deforms according to the Kirchhoff-Love assumptions. It means that the straight lines normal to the mid-plane do not change their lengths and remain straight and normal to the mid-plane after deformation.

It is possible to split the generical deformation ε in two components: the mid-plane deformation and those associated with the mid-plane curvature $\underline{K}$, that is:

$$\underline{\varepsilon} = \underline{\varepsilon_0} + z\underline{K} \Longrightarrow \begin{bmatrix} \varepsilon^x \\ \varepsilon^y \\ \gamma^{xy} \end{bmatrix} = \begin{bmatrix} \varepsilon_0^x \\ \varepsilon_0^y \\ \gamma_0^{xy} \end{bmatrix} + z \begin{bmatrix} K^x \\ K^y \\ K^{xy} \end{bmatrix} \tag{12}$$

Below is the classical approach to the mechanical modelling of laminates described in detail in the work of W. A. Stein [6]. In (Fig 7) it is shown the variation of the value of a generic component of the vector $\underline{\varepsilon}$ with respect to the variation of the coordinate z, normal to the mid-plane. The linear dependence is preserved along the laminate thickness, since the curvatures are constant by definition.

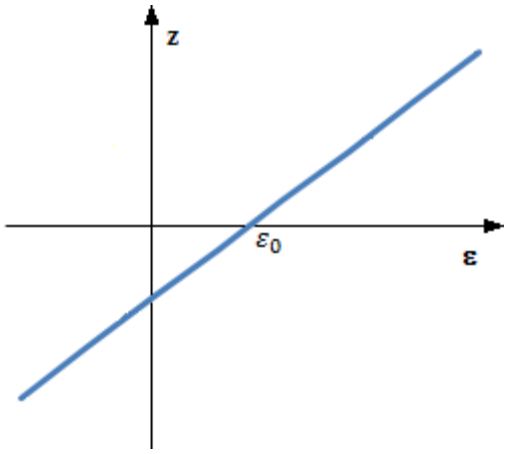

Fig 7: Linear relation ε-z

Considering a laminate of thickness *2h* with the origin placed in the mid-plane the lower surface is placed in *z=-h* and higher is placed in *z=h*. In this case it is possible to define the following values:

$$N^x = \int_{-h}^{h} \sigma^x \, dz \quad ; \quad N^y = \int_{-h}^{h} \sigma^y \, dz \quad ; \quad T^{xy} = \int_{-h}^{h} \tau^{xy} \, dz \tag{13}$$

The N^ivalues are forces per unit length. Compacting these values $\underline{F}$ it is possible to find out the following relation for a laminate made of n laminas:

$$\underline{F} = \begin{bmatrix} N^x \\ N^y \\ T^{xy} \end{bmatrix} = \int_{-h}^{h} \underline{\sigma} \, dz = \sum_{i=1}^{n} \left(\int_{h_i}^{h_{i+1}} \underline{\sigma} \, dz \right) \tag{14}$$

Taking into account the constitutive equation of a single layer (11) previously calculated:

$$\underline{F} = \sum_{i=1}^{n} \left[\int_{h_i}^{h_{i+1}} \underline{\underline{Q_i}} \left(\underline{\varepsilon_0} + z\underline{K} \right) dz \right] = \sum_{i=1}^{n} \left[\underline{\underline{Q_i}} \underline{\varepsilon_0} (h_{i+1} - h_i) + \underline{\underline{Q_i}} \underline{K} \frac{h_{i+1}^2 - h_i^2}{2} \right] \tag{15}$$

Defining the matrices $\underline{\underline{A}} = \sum_{i=1}^{n} \underline{\underline{Q_i}} (h_{i+1} - h_i)$ and $\underline{\underline{B}} = \sum_{i=1}^{n} \underline{\underline{Q_i}} \frac{h_{i+1}^2 - h_i^2}{2}$,it can be wrote in compact way:

$$\underline{F} = \underline{\underline{A}} \, \underline{\varepsilon_0} + \underline{\underline{B}} \, \underline{K} \tag{16}$$

Are defined the following momenta per unit length:

$$M^x = \int_{-h}^{h} \sigma^x \, z \, dz \quad ; \quad M^y = \int_{-h}^{h} \sigma^y \, z \, dz \quad ; \quad M^{xy} = \int_{-h}^{h} \tau^{xy} \, z \, dz \tag{17}$$

It is possible, like before, compacting in an array $\underline{M}$ and with the same process it results:

$$\underline{M} = \sum_{i=1}^{n} \left[\underline{\underline{Q_i}} \; \underline{\varepsilon_0} \frac{h_{i+1}^2 - h_i^2}{2} + \underline{\underline{Q_i}} \; \underline{K} \frac{h_{i+1}^3 - h_i^3}{3} \right] \tag{18}$$

Defining the matrix $\underline{\underline{C}} = \sum_{i=1}^{n} \underline{\underline{Q_i}} \frac{h_{i+1}^3 - h_i^3}{3}$, it can be wrote:

$$\underline{M} = \underline{\underline{B}} \; \underline{\varepsilon_0} + \underline{\underline{C}} \; \underline{K} \tag{19}$$

In this way it results the following constitutive equation:

$$\begin{bmatrix} \underline{F} \\ \underline{M} \end{bmatrix} = \begin{bmatrix} \underline{\underline{A}} & \underline{\underline{B}} \\ \underline{\underline{B}} & \underline{\underline{C}} \end{bmatrix} \begin{bmatrix} \underline{\varepsilon_0} \\ \underline{K} \end{bmatrix} \tag{20}$$

The matrices $\underline{\underline{A}}$, $\underline{\underline{B}}$ and $\underline{\underline{C}}$ depend via $\underline{\underline{Q}}$ from the reference adopted.

By means of this approach the laminate constitutive equation is defined in very simple and compact form and it contains the information about the constitutive equations of each lamina, so it is very useful especially in computer aided calculation and design thanks to the strong possibility to automate the construction of the model.

2.5 Material classification

In this section, they will be listed the materials most commonly used in the production of composite and their most relevant characteristics will be briefly described.

2.5.1 Fibers

❖ **Glass fibers**

There are different types of glass, which are distinguished according to the composition of the starting mixture and the use to which they are destined [10]:

- E Glass: good mechanical properties, good corrosion resistance and it is transparent to electromagnetic waves;
- C Glass: very resistant to chemical agents;
- M Glass: for uses requiring a high modulus of elasticity;
- D Glass: has a low dielectric constant and good mechanical properties;
- L Glass: fibers for anti-radiation materials;
- S or R Glass: high mechanical strength, widely used in the aeronautical field.

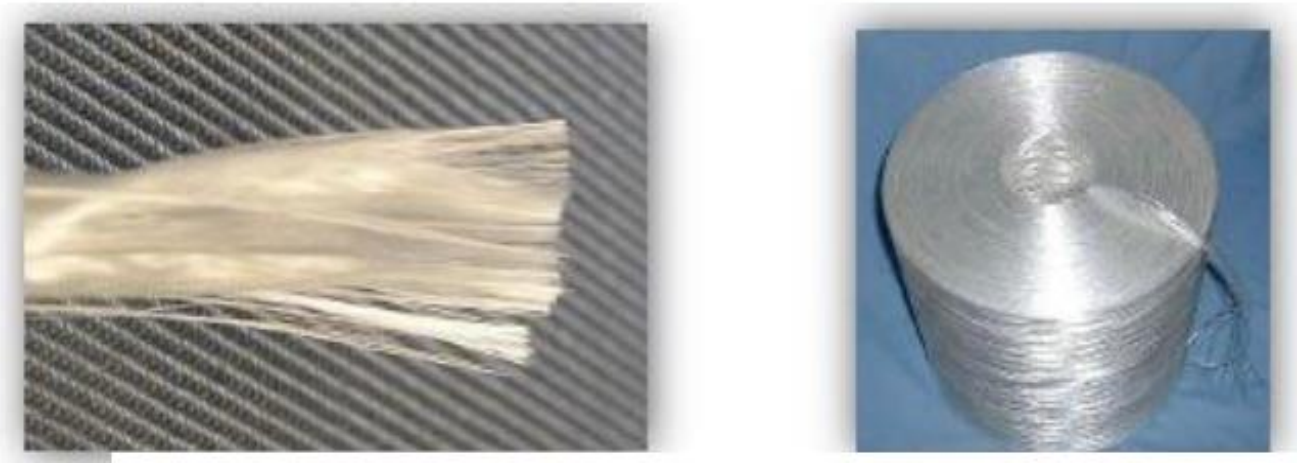

Fig 8: Glass fibers

The fibers (Fig 8) obtained by drawing, are rather long and chemically treated to improve the flowability characteristics at the interface with the matrix. They are then wound to coil (Fig 8) and marketed.

The glass fibers have positive characteristics as a low production cost, high mechanical strength and low density. The disadvantages, however, are the relatively low modulus of elasticity that involve high deformations under the application of loads.

❖ **Carbon fibers**

These fibers have, of course, carbon as the main constituent. The finished product is made up of bundles of fibers (Fig 9). This kind of fibers are very used in the aeronautical field because of the low specific weight, the low thermal expansion coefficient, the high mechanical resistance and the high mechanical rigidity. One of the main problems of the carbon fibers is that its yield point is very close to the breaking point, therefore there are not visible alterations of the structure when the load approaches the breaking point. Another problem that limits its use is its cost [10],[12].

Fig 9: Carbon fibers

❖ **Aramid fibers (Kevlar)**

The types of Kevlar more marketed:

• Kevlar 29 for its shock resistance

• Kevlar 49 for the high mechanical rigidity and considerable mechanical resistance (intended to structural components)

These fibers (Fig 10) good resistance to corrosion, do not melt, carbonize at 500 ° C, do not have electric conductivity, and the cracks propagate with difficulty. [11]

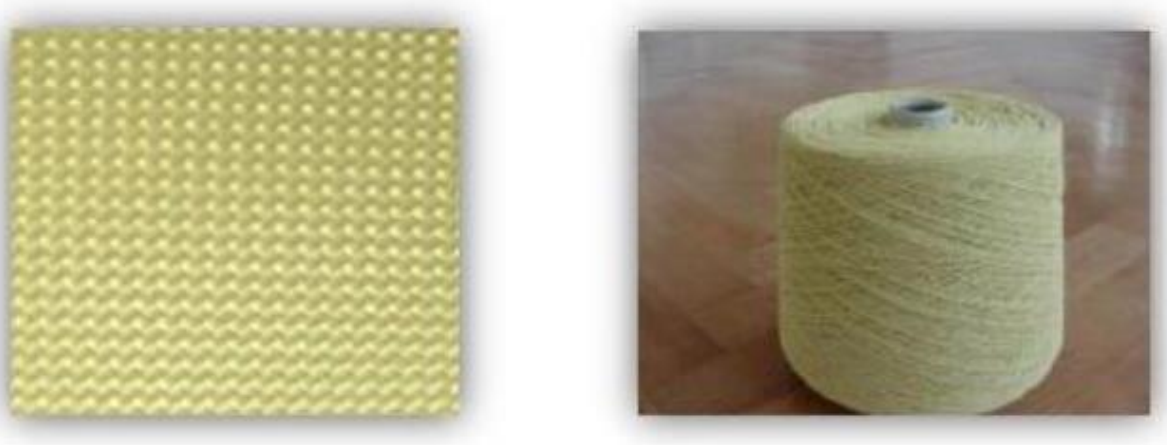

Fig 10: Aramid fibers

❖ **Boron fibers**

Even this type of fiber is wrapped in coils on the market. The technology of boron fibers, however, is very expensive and this together with the high density of the material has led to a substantial abandonment [10].

❖ **Silicon carbide fibers**

They are characterized by ceramic nature and, therefore, by high mechanical strength; They are also transparent to electromagnetic waves in the radar band. Such fibers can be long and oriented, short and compact or in the form of whiskers (very fine fibers) and distributed uniformly in the

light alloy matrix aluminium, allow to obtain a rigidity increase of 50% compared to that of the base metal material. In this feature, however, it adds a certain fragility due to a low deformability.

2.5.2 Matrices

Between the two phases that constitute the composite, the one that characterizes the type, relative to the field of possible applications, and therefore may be taken as reference to the classification of the material, is the matrix. The matrices can be of different types and classified according to the value of the maximum temperatures of use, to which can be adoperate without having to undergo degradation phenomena.
In the following a description of the main types of matrix operating today is given.

- **Metallic matrices**

The most significant problems in the use for such matrices are related to the interface with the fibers, which requires the use of metals that are liquid at temperatures not compatible with the integrity of the fibers. They can also generate chemical reactions with formation of compounds that can damage the fibers. To facilitate the operation and to avoid damage, the metal penetration occurs by atomic-metal diffusion in the solid phase without reaching the melting temperature. The metal is interposed between the fibers in the form of powders or thin sheets. Dangerous chemical reactions are removed by treating chemically the surface of the fiber. These materials are still experimental, but the most promising for future developments are the composite of graphite-aluminium and graphite -magnesium [10], [8], [5].

- **Ceramic matrices**

The ceramic matrix materials are very promising, especially in the trans-atmospheric field, characterized by high temperatures. The best matrices are those consisting of oxides, borides, nitrides, which solidify in the crystalline or glassy state. Other constituents are aluminium Al2O3 and mullite, composed of aluminium, silicon and oxygen. Such refractory substances, hardly fuses, are formed by sintering of the constituents in the form of powders ceramic powders. Matrices made have high stiffness and mechanical strength, good creep resistance at high temperature and the raw materials they are also inexpensive. It is also thought to fabricate ceramics mechanical parts which, however, have a high fragility. To solve this problem, it strengthens the matrix with filaments composed of ceramic material (silicon carbide fibers). The fibers can improve the fracture resistance, blocking the propagation of the defect. The material obtained remains usable over 1500 ° C, due to its toughness. The ceramic composites are studied to be used in the construction of hot parts, the operation of which takes place at temperatures of the order of more than 1000 ° C: components of automotive and aeronautical engines, exhaust nozzles and coating structures, such as the nose and the edges of the space shuttles attack [10], [8], [5].

- **Polymeric matrices**

The polymer matrix composites are the most widespread and have been developed to improve the mechanical strength of the polymer even when temperature increases, while maintaining the features of lightness. They are divided into organic and inorganic. The most important of the

former are the epoxy resins. The epoxy group is found in some polymers obtained by adding epoxides and phenols such as bisphenol and epichlorohydrin. The polymer obtained is in the form of viscous fluid. To obtain the condensation by polymerization of the resin it must be added with the hardener, consisting of amines (containing the amino group NH_2), having the function of catalyst of the chemical reaction of polymerisation. The solidification phenomenon of such resins is rather complex. From a chemical point of view, the hardening can take place at environmental temperature with very long times, by the removal of water via a crosslinking reaction. The industrial hardening process is carried out at elevated temperature by means heating. The parameters that influence the phenomena are the treatment temperature and the duration time. The product that is obtained has good mechanical properties, excellent adhesion capacity to the fibers and low shrinkage in the liquid-solid state transition. A drawback is given by the phenomenon of absorption of small amounts of water that degrade the characteristics of resistance to compression and shear. These resins are used particularly with glass and carbon fibers [10], [8], [5].

There are several families of resins which differ the one from the other according to the different chemical composition, which has repercussions on the physicochemical properties of the materials.

It follows a list of the main families of resins [10]:

- Thermoset:
    - Phenolic;
    - Amide;
    - Epoxy;
    - Polyurethane;
    - Silicone;
    - Alkyd;
- Thermoplastics:
    - Acrylic
    - Polycarbonate
    - Thermoplastic polyester
    - Polyvinylidene fluoride
    - Polyolefin (polyethylene, polypropylene)

❖ **Thermoset resins**

These resins during the production process undergo irreversible chemical transformations that make them insoluble and infusible. This transformation is associated with the creation of covalent crosslinks, during the polymerization process. The most important thermosetting resins, both from a strictly historical point of view and from the point of view of the current commercial applications, are those obtained from reactions of polycondensation of formaldehyde with phenol (phenolic resins) or with urea or melamine (amide resins). Other important classes of thermosetting resins are epoxy, urethane foams, the polyester unsaturated resins, silicone resins, alkyd resins and other minor importance. In the production of composites are used in a state of monomers or low viscosity oligomers, which react irreversibly to form a highly crosslinked

structure. All the thermosetting resins have an exothermic polymerization reaction, which means that during the polymerization reaction develops heat and the amount of heat developed depends on the mass, which then cannot be excessive since it could cause the destruction of the resin itself. The temperature helps the reaction since while it increase reduces the reaction time, then the monomers bind faster. After reacted, the polymer is no longer reformable and can be processed only once [8], [5].

❖ **Thermoplastic resins**

In the production of composites are used in a state of high molecular weight polymers that can be melted, consolidated and then cooled. Not chemically crosslink with heat and therefore do not require long cure cycles. For the processing will require high temperatures and pressures due to their high viscosity. They can be recast for subsequent forming or assemblies. The thermoplastic resins are linear or branched polymers that can be melted by providing them an appropriate amount of heat; during the step of plasticizing does not undergo any change in the chemical level. They can be forged (and reshaped) in any form, using techniques such as injection molding and extrusion. Through the heat is obtained the fusion of these polymers which, subsequently, in contact with the mold walls, cooling to solidify [8], [5].

2.6 Polymerization process

One of the final stages of the manufacturing process of a composite material with a thermosetting matrix, consists in subjecting the fiber-matrix mixture at a predefined thermal, having the purpose of triggering and supplying a chemical reaction, exothermic and irreversible, called cure. The amount and the duration of the set temperature variation, relative to the cycle of care, represent the basic parameters of the process, which affect the distribution of temperature and the progression of the exothermic reaction. The manufacturing process of a composite material components, is characterized by very different problems, because there are many phenomena to be monitored, to determine the best mechanical and physical characteristics of the material, depending on the performance which it has to offer. The success of a cycle of treatment depends on its capacity to provide a good product, or a product that meets the physical, chemical and geometrical requirements set out in the planning phase. The problems be divided into two fundamental aspects of the manufacturing process: the obtaining of the desired geometry with the consequent mechanical constraint conditions which must be realized (molds), the fiber-matrix integration with the simultaneous polymerization of the latter [7].

In brief, the process involves at least the following phenomena:

- chemical polymerization and cross-linking reactions;
- development and transmission of heat;
- viscosity and viscoelastic behaviour;
- voids presence and degassing.

❖ **Mechanisms of polymerization**

With the term polymerization refers to the chemical reaction that leads to the formation of a polymer chain, or a molecule made up of many equal parts, called "monomers" or "repeating units", which are repeated in sequence.

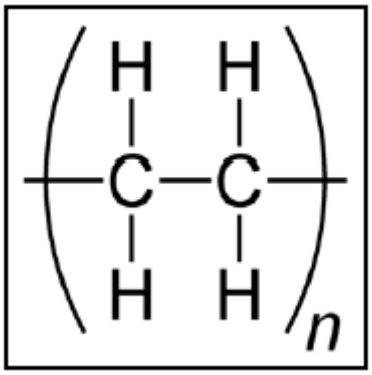

Fig 11: Polyethylene molecule, [8]

In 1929 the polymers were distinct from Wallace Carothers in addition polymers and condensation polymers, depending on whether the polymerization reaction produces, respectively, only the polymer or even a species of low molecular weight called "condensed" (for example, H_2O). Later in 1953, Paul Flory distinguished the polymers according to the reaction mechanism followed by the polymer synthesis reaction. Depending on the reaction mechanism, the polymerization reaction can in fact be divided into:

- chain polymerization
- step polymerization

The polymers obtained by step polymerization are generally condensation polymers, while the polymers obtained by chain polymerization are typically addition polymers.

In the chain polymerization the reaction is triggered by the formation of an active chemical species, call initiator, which can be constituted by a radical (a group of atoms with an unpaired electron). The initiator sum recursively upon himself a monomer molecule, moving the center of reactivity (the unpaired electron) at the end of a chain that gradually it grows. The production process of a polymer chain is divided into 3 phases: activation, propagation, and termination. An example of a polymer obtained by this reaction is the polyethylene: the molecule is represented by the unit and a repetitive number "n" (Fig 11), which indicates the number of repeating units of which is composed of the polymer. The step polymerization is carried out between chemical species having two or more reactive ends, then capable of binding to each other, forming long chains for union of shorter chains [7].

❖ **Cure cycle**

The manufacturing process of polymer matrix composites is completed subjecting the material to a thermal cycle such as to trigger and supply, inside the resin , the exothermic chemical reaction of cure. The thermal treatment consists in bringing the resin to its curing temperature, by means of a suitable thermal profile characterized by a sequence of rises and stays at a characteristic temperature. Final specifications of the product depends significantly from this phase of the process.

The goals can be summarized in three points:

- Resin Curing up to a certain degree of reaction of approximately 0.9 - 0.95;
- Removal of excess resin and compacting the laminate;
- Removal of the gas and control of the voids in the resin.

The characteristics of the manufacturing process in which the matrix and the reinforcing phase are combined to form the composite, are the determining factors for the realization of a superior properties material. In it the matrix plays a very important role, since it undergoes physical and / or chemical changes as a function of time and temperature during the process, and also governs the viscoelastic properties of the composite. The wide range of matrices that can be used provide a complex assembly process variables and final properties of the composite, which can be modelled through the application of fundamental principles of the transport of matter, momentum and energy on a multiphase system with time-dependent properties [7].

❖ **Variables of the cure process**

As previously stated, there are many variables that determine the final characteristics of a composite material. The principal will now be briefly described, specifying their areas of influence.

- Temperature
  The temperature affects the reaction kinetics *id est* on the reaction rate. It has influence on the viscosity and involves if not controlled degradation of the resin.
- Degree of cure
  The degree of cure involves an increase of the molecular weight and the evolution of the viscosity, in addition to development of heat and at a high degree of crosslinking.
- Viscosity
  The viscosity affects several factors such as the capacity of impregnation of the fibers, the removal of the gases from the resin, the resin flow on the fibers, the consolidation of the laminate.
  An empirical relationship is as follows:

$$\mu = \mu_{\infty} * exp\left[\frac{E_a}{RT} + k\alpha\right] \tag{21}$$

  In which μ_{∞} is a constant, E_a is the energy of activation of viscous flow, α is the degree of cure and k is a constant independent of temperature [7].

❖ **Stages of cure**

Depending on the temperature and the reaction progress state, the resin may be in three different phases:

- Liquid phase
- Rubbery phase
- Glassy phase

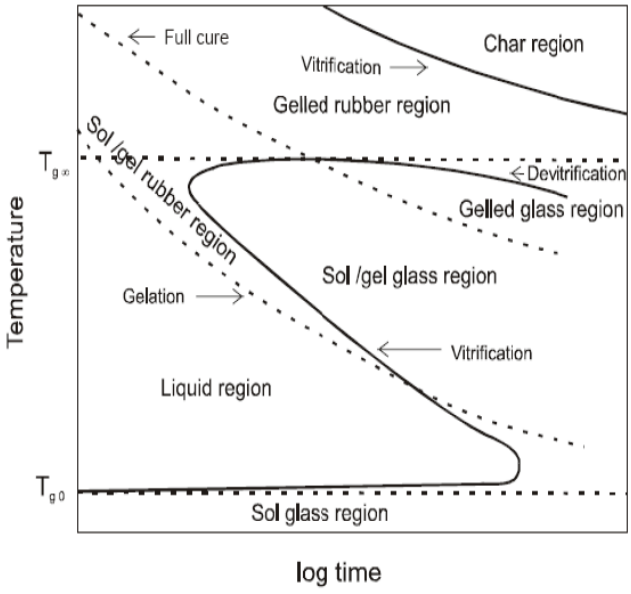

Fig 12: TTT diagram for resin's cure, [7]

In (Fig 12) it is shown the TTT diagram (Temperature, Time, Transformation), by which it is possible to identify the state of the resin to the progress of the polymerization reaction, according to the thermal profile below. With reference to the diagram, depending on the position with respect to the vitrification curve (vitrification), a couple of temperature and time values can identify a liquid resin (liquid region), a gelled resin (gelled rubber region) or a vitrified resin (sol / gel glass region). In addition to the vitrification curve also shows the curves of gelling (gelation) and of complete cure (full treatment). The complete cure curve is a curve of type iso-degree of cure. The area called char region is representative of the maximum temperature reachable during the resin processing, beyond which it would get the carbonization thereof.
In the diagram, two characteristics temperature are also indicated:

- The temperature T_{g0} that represents the glass transition temperature of the cured resin (degree of cure null). It is also said pre-preg storage temperature, since for greater-equal temperature the resin is always located in the glassy phase and the polymerization reaction is so slow that it can be considered firm (sol glass region);
- The temperature $T_{g\infty}$ represents the glass transition temperature, in correspondence of which there is the complete polymerization (degree of cure unit).

While increasing the degree of cure α the resin phase can change, depending on the temperature, through the curves of gelation and vitrification. It is possible to have the transition from the liquid to the glassy state, from the liquid state to the rubbery state and from the rubbery state in the glassy state.
To achieve the vitrification, i.e. to obtain a stable glassy solid is to be effected a cooling in such a way as to intersect the vitrification curve and arrive in the sol / gel glass region. The reaction which leads to cross the vitrification curve is reversible. The vitrification curve can in fact be crossed in both directions: lowering the temperature can go from a rubbery material to a vitrified material and vice versa starting from the vitrification zone citing temperature, is possible to pass from a glassy solid to an elastomer. Consequently, the temperature $T_{g\infty}$ defines the upper limit of the composite utilization realized. The TTT diagram with the curves relating iso-degree of cure shows how, with the increase of the treatment temperature, increases the speed with which you can reach higher and higher degrees of polymerization to the advantage of processing times. Conversely, as the temperature increases, it decreases the time during which the resin is characterized by a viscosity such as to allow an optimal impregnation and a removal of excess resin, before that the reaction leads to gelation and then to vitrification [7].

❖ Polymerization measurement techniques

For characterize the progress of the cure reaction it is possible to use different models, which are grouped into two categories depending on the parameter analysed:

- chemical analysis methods;

- Physical methods of analysis.

Among the most common chemical methods include the infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), liquid chromatography (HPLC) and radio-chemical methods. Among

the physical methods will instead include the differential scanning calorimetry (DSC), the thermal scanning rheometry (TSR), the thermo-mechanical analysis (TMA) and dynamic mechanical analysis (DMA) [7].

2.7 Impregnation process

An important parameter of the impregnation process, results to be the permeability of the reinforcement. The perfect adhesion between fiber and matrix is one of the most important parameters for the success of the entire production chain.

To understand the behaviour of the flow of resin through the reinforcement, many researchers have conducted studies to achieve mathematical models that were describing and would explain this phenomenon, evaluating of the permeability coefficient in function of the properties of the fluid, of the reinforcement structure, and the fibers volumetric ratio.

These models are based largely on Darcy's law, which describes the macroscopic flow of a fluid through a porous medium under the assumption of incompressible resin (Newtonian fluid and low Reynolds number);

Darcy's law can be written in the form:

$$Q = \frac{K * \Delta P * S_P}{\mu * L} \tag{22}$$

where S_P is the area of the passage section, L the length of the fluid path, μ the fluid viscosity and K the permeability which, in general, varies depending on the type of working fluid used (Newtonian or not).

Some studies have reported that the flow behaviour of a Newtonian fluid in the impregnation conditions of saturated and unsaturated differs from Darcy's law, because the permeability is a function of the porosity, the surface speed and the pressure drop. Through these studies, it is then evaluated the dependence of permeability from surface speed even at low resin injection pressures, where both inertial phenomena that the deformation of the reinforcement are negligible, explaining the phenomenon with the interaction between macro and micro flow. The reinforcement creates a double porosity due to the presence of voids between the fiber bundles, hence there are two flows within the impregnation process, a macroscopic flow, which affects the regions between the fibers, and a microscopic flow, that affects the inner part of the fibers. These flows lead to the identification of two regions, termed saturated (in which the fibers are completely impregnated) and unsaturated (in which the resin has filled the voids between the fibers but does not completely impregnated the fiber). If the resin flow between the voids is faster than the process of absorption in the fiber bundles, this implies that of air remains trapped in the fiber bundles. The air trapped in the fiber bundles affect the continuity equations. However this problem is eliminated in those technologies that produce a vacuum in the cavity in which the resin will be injected [7],[8].

2.8 Fiber-matrix interaction

To define the typical characteristics of a composite is necessary to identify those of its constituents and in particular the way in which they interact. The fibers are constituted by resistant solid bodies of elongated shape, having longitudinal dimension prevalent with respect to the cross dimension, and have the task of providing strength and stiffness to the composite. The matrices have, instead, the task to run from the filling material. Initially in the state of the viscous fluid in order to fill all the spaces and perfectly adhere to the fibers, the matrix undergoes a solidification process which allows to give stability to the structure and geometry, then adhering to the fibers allows transferring the external loads applied. This transmission takes place by means tangential stresses. This allows the material to receive the external stresses, due to the applied loads, redeploying them to the fibers in the form of internal stresses. This shows that the matrices have not structural tasks, but loads transfer task.

The behaviour of a composite under load, in which a breaking crack is propagating, is rather complex. Initially the crack affects the matrix and then propagates to some fibers, causing damage, breakage or put out of action. The behaviour of the fibers assumes, therefore, a very important role that determines the greater or lesser capacity of the composite to withstand external loads, blocking, retarding or favouring the propagation of the crack. Comparing long and short fibers with equal resistant section it is possible to notice that the long ones reinforce the composite more than short ones. It is also useful to design the internal geometry of the composite orienting the fibers according to the maximum stress directions. To achieve continuity and resistance characteristics gather the fibers in bundles, in the form of wires in parallel fibers or twisted. In (Fig 13) is represented the resistant behaviour to a breaking crack by short fibers randomly arranged.

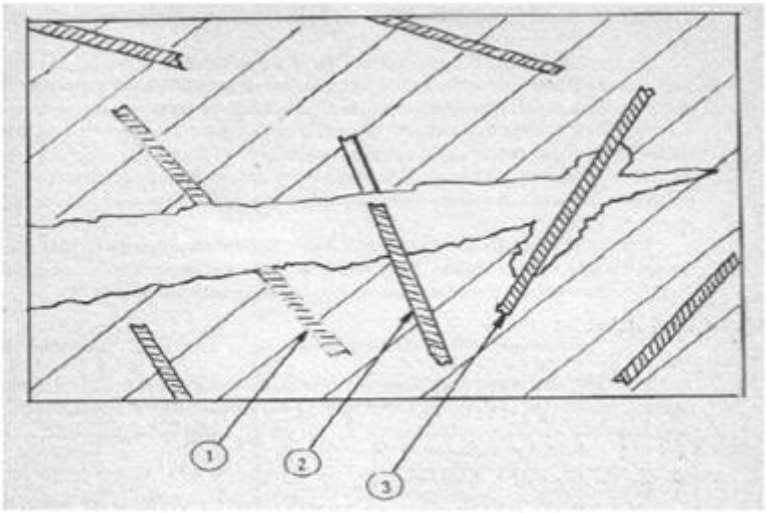

Fig 13: Crack propagation in a short fibers composite, [12]

In (Fig 13) there are the ways in which the fracture can occur:

1. Rupture of the reinforcement fibers.
2. Ouster with extraction by detachment of the fiber from the matrix.
3. Separation of the fiber from the matrix for failure of the latter in the contact zone.

In the first case, the stress has exceeded the maximum load sustainable by the single fiber. The phenomenon can be avoided by increasing the number of fibers or changing the size or type.
In the second case, the fiber is no longer able to oppose, in a valid way, the
release stress. It is then extracted completely, lacking the adhesion between fiber and matrix.
In the third case, the fiber is able to exercise a minimum of reaction to external stress, being still partially in place [7],[8].

2.9 Main manufacturing process

A production process has to ensure cost-effectiveness and compliance with the following conditions:

- Give proper orientation to the layers of overlapping fibers, respecting the part geometry
- Observe the conditions of temperature and pressure of the polymerization process, and made minimum levels of internal porosity and the required degree of surface finish.

The choice of the most convenient method depends on two factors:

- Geometry and the size of the piece to be built
- Structural resistance features that the piece should possess in work.

The current production of polymer matrix composites, is moving from a period in which the applications were mainly oriented to high value-added niches (aerospace and aeronautical etc.), To a phase in which are wanted less sophisticated applications and mass production in sectors such as automobiles and public goods. To ensure that the high-performance composite materials can spread in these fields, it is necessary to reduce production costs, to obtain finished materials and parts can be produced with constant quality and in an economical manner. Since currently the cost of processing accounts for about 60% on the cost of a piece of composite material, it is easy to identify the field where it is necessary to intervene. To reduce costs it is necessary face two major problems, the first is the reduction of waste, and the second is control of the process and its optimization. Currently there are few manufacturing processes of composite materials that allow full control of the process, and are exceedingly few data available to carry out this monitoring. During the production process of polymer matrix composites, occur several physic-chemical phenomena which include: chemical reactions, crystallization processes, heat exchange and flow. Therefore, to fully describe such a process, it is necessary first to make a complete characterization of materials and describe, at least phenomenologically the processes taking place. This study may be performed experimentally in the lab, creating behaviour patterns able to simulate the processes themselves. By operating this type of approach is possible in the production stage, optimize the processes being able to produce parts of consistent quality, with reduction of rejects and increase of production cost effective.
The production technologies of composite materials vary mainly according to the application and to the characteristics, geometric and mechanical characteristics of the final product.
It follow a short description of the most common manufacturing process of composite materials [5], [8], [10].

❖ **Manual lay-up**

It 'a still widespread process for work on large surfaces such as swimming pools and hulls of boats, for which the production is typically carried out for small lots or lot unit. The fiber reinforcements are laid out inside the mold in the form of strands or fibers of fabrics. The fibers are then impregnated with catalysed resin and consolidated manually using brushes, metal or plastic rollers or spray guns (Fig 14)

Although widely used, this manufacturing technology has considerable disadvantages for the workers in terms of safety. In fact the reactions that take place during the polymerization of the resin, may release into the work environment various harmful substances [10].

Fig 14: Manual lay-up

❖ **Spray lay-up**

Spray lay-up is an open-moulding composites fabrication process where resin and reinforcements are sprayed onto a reusable mold. Fibre is chopped in a hand-held gun and fed into a spray of catalysed resin directed at the mould. The deposited materials are left to cure under standard atmospheric conditions. This process is very simple and very economic, but it is impossible to set exactly the amount of resin [10].

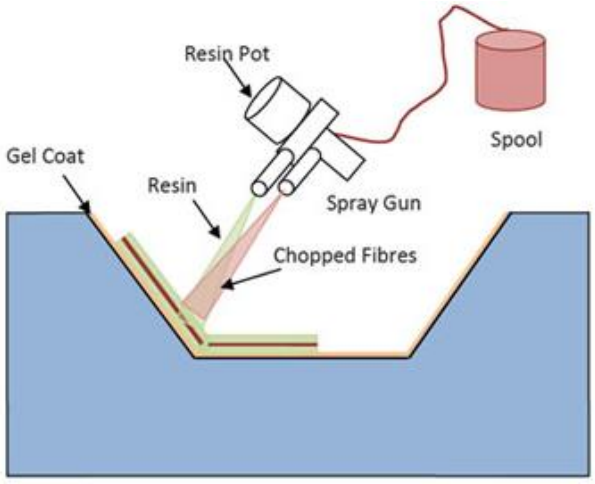

Fig 15: Spray lay-up, [10]

❖ **Vacuum bag moulding**

Vacuum bag moulding uses a flexible film to enclose the part and seal it from outside air. The lay-up is completed and placed inside a bag made of flexible film and all edges are sealed. The bag is then evacuated, so that the pressure eliminates voids in the laminate, forcing excess air and resin from the mould. With this process it is possible to obtain very resistant laminate.

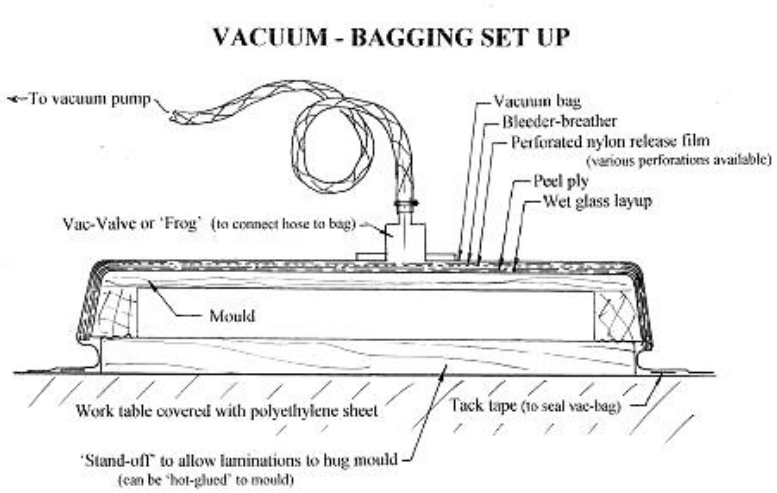

Fig 16: Vacuum bag moulding, [12]

❖ **Forming in a mold in autoclave**

It is used for the extended surface artefacts, flat or curved and open form. In this process the basic raw material endeavoured is constituted by the fibers and the potting resin, generally the organic polymer. Production is carried out placing on open molds the resin impregnated fiber layers; subsequently the molds are introduced in autoclave (Fig 17), in such a way as to subject the material to a polymerization process to certain pressures and temperatures [10].

Fig 17: Forming in autoclave, [12]

❖ **Compression molding**

The products of limited dimensions and of simple shape that is complex, can be manufactured by using the compression in the press between mold and counter mold, with relative polymerization. This compression ensures a good compaction of the composite, with the expulsion of the air and of the gases that may give very harmful internal blowholes [10].

❖ **Resin Transfer Molding (RTM)**

The RTM process (Resin Transfer Molding) is one of the most attractive and efficient processes, for the production of polymer matrix composite materials with high performance at low manufacturing costs. Reinforcement mat or woven roving is placed in the mold, which is then closed and clamped. The resin is pumped in under pressure, displacing the air and venting it at the edges, until the mold is filled. The resin cures at low temperature and low pressure. This process is suitable for medium volume production of larger components. It is recommended for products with high strength-to-weight requirements [10].

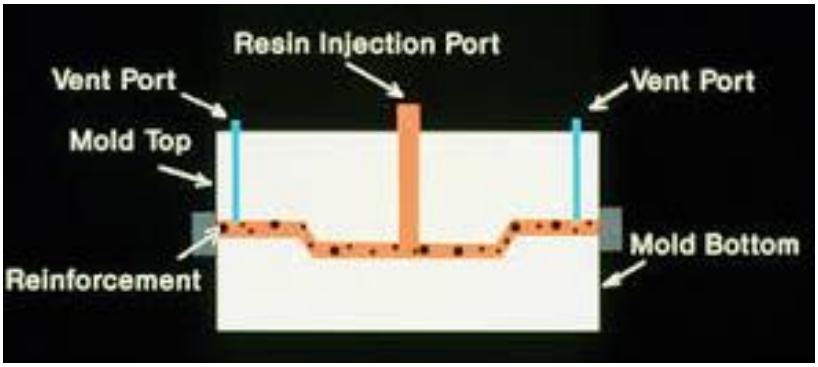

Fig 18: Resin transfer molding, [10]

❖ **Filament winding**

This technique is optimal for realizing parts characterized by a circumferential trend of the reinforcement , such as pipes, oil ducts, pressure tanks or parts of strong elongation in cross-section but not circular, such as aerofoils for the helicopter blades. The processing is carried out by winding machines (Fig 19), in which an appropriately shaped mandrel is rotated by an electric motor. At the same time one or more tapes are held from rotating coils on spools, which are placed on fixed frames at a certain distance from the machine and during the winding takes place the polymerization phase.

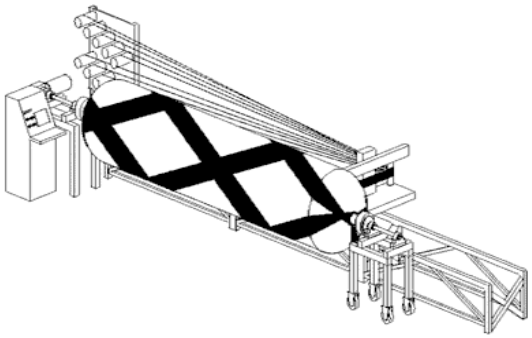

Fig 19: Filament winding, [10]

3. Pultrusion process

3.1 Introduction

Pultrusion is a continuous production process of constant cross-section composite material parts. It is, as can be deduced from the name, an extrusion process driven by a pulling action.
The pultrusion process enables the production of manufactured components characterized by an alignment and uniformity of distribution of almost perfect fibers and by a high reinforcing rate (expressed as a percentage of the volume of the total volume fibers), not reachable by any other technology. Normally a pultruded part has a variable reinforcement rate of between 50% and 60%, which is about the double of what can be achieved with manual layout techniques. Furthermore, the rates of reinforcement achieved and, therefore, the final performance of the final composites, are controllable with high precision. The combination of good mechanical properties (high elastic modulus and tensile strength) with excellent corrosion resistance properties (and in particular to chemical pollutants) makes the pultruded parts suitable for use in a wide range of applications [8], [11], [12].

3.2 Process description

Pultrusion is a continuous process which allows to obtain profiles of any length in composite material. Among the various processes of production of composite objects, the pultrusion is classified within the closed mold processes group. The fibers, initially wounded around the bobbins of a creel, are generally guided first in a tank, in such a way as to be impregnated by a thermosetting resin and then through the preforming system (there are also a process variant which provides for the use of thermoplastic resin, but in this case are used directly prepreg).

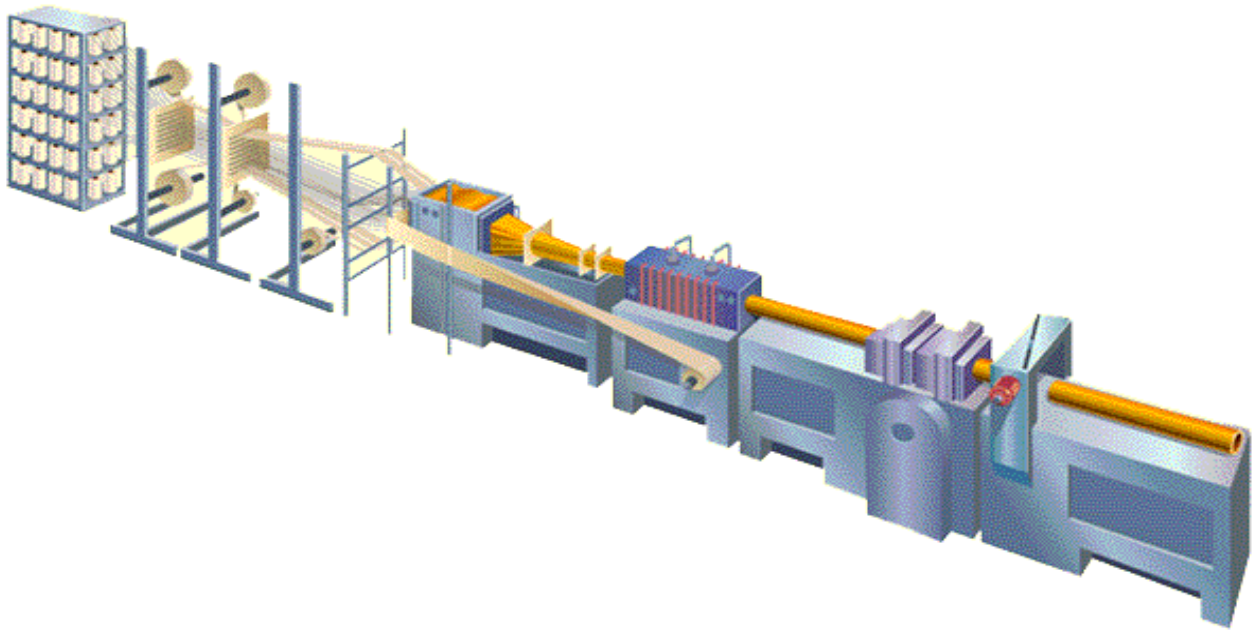

Fig 20: Pultrusion process, [11]

Then there is the passage through the heated mold, wherein the resin cure step takes place. Then, after a cooling phase in the post-mold portion, the composite solidified pass by the pulling system and, finally, the cutting system, which allows to obtain the desired length of the profiled element, without interrupting the continuity of the process. Everything is monitored through a control panel. It follows next a more detailed description of the basic components of the process [11].

- **Creel racks and guiding system**

The creel racks is a storage system of yarns which allows a rapid and continuous sorting of the fibers to the resin baths. It consists of a battery of bobbins that can vary in number, depending on the magnitude of the process, even reaching 1000 units. Wound around these bobbins are the coils of roving or mat (depending on the geometry that is being sought) of glass and, less frequently, also aramid or carbon coils. The bobbins are arranged in such a way as to be easily unrolled, that is, so as not to create resistance to the pull necessary to carry the fibers through the next resin bath and then through the remainder of the pultrusion line. Furthermore, in the arrangement of the coils on the bobbins care is taken to avoid the friction between the fibrous filaments, greatly lowering the risk of the formation of a considerable electrostatic charge and lowering the possibility of formation of ripples, which in the resin bath result in a viscosity increase. In order to further minimize the risk of having problems of electrostatic nature, they are generally adoperate metal racks, allowing the connection to the grounding system, so as to dissipate the static charge. The guides, placed immediately after the creel rack, consist of perforated plates, positioned slightly above with respect to the pull center of the coils and having the task of properly orient the fibers directed toward the tank used the resin bath. The eyelets of such plates are of ceramic material (generally of porcelain), that resists wear resulting from contact with the fibers, in order to eliminate the electrostatic accumulation and degradation of the glass. A variant of the guidance system provides the use of a more elementary of vinyl tubing system, in place of the above ceramic plates, preventing rippling of the fibers [11].

- **Impregnation tank**

The impregnation tank is a component present in most widespread variant of pultrusion, i.e. one that provides an off-line bath. The off-line version requires that the fiber impregnation occurs before of the preform, instead in the on-line one takes place during forming. With regard to the process variant which provides an on-line bath, the impregnation tank obviously has no more reason to be endeavoured. The same is true in the pultrusion of thermoplastic prepregs. This tank is nothing more than a metal sheet pool containing the liquid resin mixture. The fibrous reinforcement must pass below the free surface level of the mix, in order to be impregnated by the mixture itself. In addition the fibers must be held, so that the impregnation takes place under the best possible conditions and are not left voids in the final composite. To facilitate the passage of the fiber under the resin layer and to further stretch the fibers, are used rollers. These rollers can be positioned all within the impregnation tank, otherwise can be distributed between the inside and the outside of the tank. In addition, some tanks are made so that the fiber impregnated escaping from the free surface of the mixture and is conducted out of the tank by means of

another roller; other pools, however, are equipped with slots: there are grilling plates that filters the impregnated fibers, removing excess resin. Other pools are equipped with grills plates at both ends of the input and the output. Another function of such grid plates, in fact, is to maintain aligned the reinforcing filaments. The resin mixture which emerges from the bath is collected and is subsequently reintroduced into the impregnation tank.

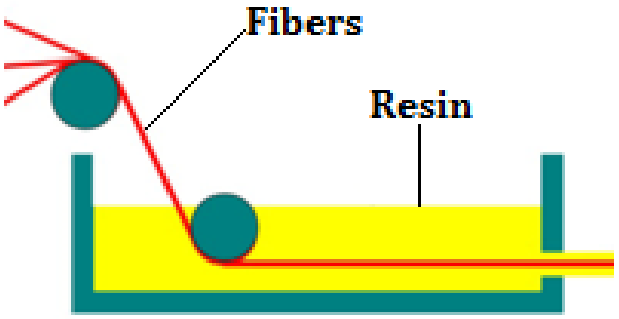

Fig 21: Impregnation tank, [12]

A problem related to this phase of the pultrusion process consists in the emission of styrene. The loss of this monomer not only leads to an increase of viscosity in the resin (and therefore to greater difficulty of impregnation of the fiber), but also to environmental concerns: a prolonged exposure of the operators to levels of styrene that exceed a certain threshold (threshold that is set by the laws of the various countries, and, in general, requires that in 8 working hours should not exceed average concentrations of several tens of ppm of styrene vapours in the working environment) can have harmful effects on their health, causing both short-term disorders (such as irritation of the conjunctiva and the nasal mucous membranes) and long-term (chronic intoxications). It is therefore necessary, in environments where there is an off-line pultrusion process, to use an adequate local ventilation, in order to maintain the level of concentration of sufficiently low styrene. This kind of environmental concerns has driven the industry of the pultrusion to search for an alternative method for the resin bath phase, considering the possibility to carry out the bathroom of the fiber in the on-line mode, i.e. inside the mold (so to keep the styrene vapours into the mold cavity). However this process variant has obvious limitations, consisting in a greater cost of equipment (need to have a reliable resin pumping system), in a lower permeability of the fibrous structure (arrived at the entrance of the mold it is now compacted), resulting in less possibility of using fillers (which would increase the viscosity, decreasing the fiber impregnation) or to work at high line speeds. That's why the bath of the off-line mode is still the most widespread option [11].

- **Preforming system**

The preforming system consists of a series of devices that allow the impregnated reinforcement, having the form of bundles of roving and / or flat layers of mat or fabric, to be collected and formed until reaching the final geometry, which allows it to be able to move to the next stage of cure in heated mold. These devices are constituted by perforated plates, which can be in polietilene or in a chrome steel: the polyethylene ensures greater ease of processing, while the chromium steel provides a longer life. These plates are placed in axial sequence; their complexity

and their number depends on the geometry of the final composite: the more complex the profile to be obtained, the more complex will be the plates (there will be multiple holes, arranged in more particular geometries), the greater the number of the plates which is taking place between the pressure tank and the mold. In figure (Fig 22) it is shown the sequence of the preforms for a double-T beam.

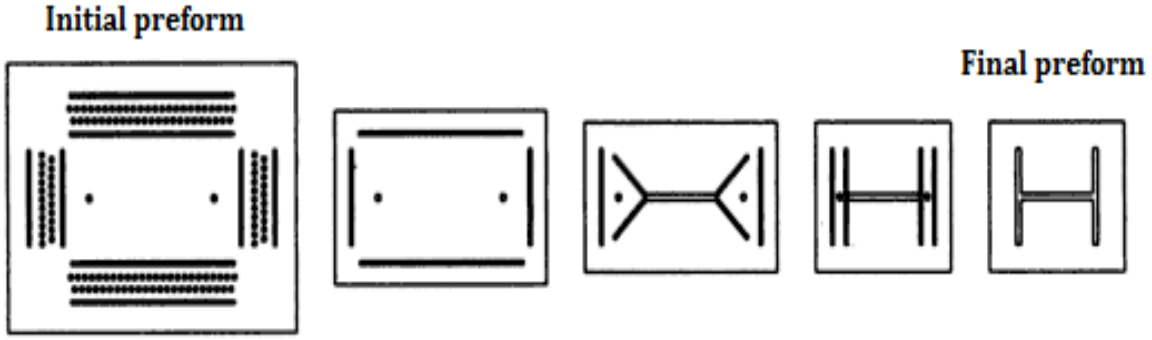

Fig 22: Preforming system for a double-T beam, [12]

Even if it is possible to find the most varied geometries of preform guides, according to the shape of the final composite, the general principle according to which the plates are build and disposed is always the same, regardless of the geometry of the profile are constructed and arranged: to realize a progressive collimation of the material (fiber and resin) in a sequence that provides the accurate positioning of the fibers and that at the same time minimize the local stresses, which, if too large, may have adverse effects on the fibers themselves (which individually are a bit more fragile). Another feature of the plates is to remove the excess resin, if this has not already been completely removed earlier in the passage of the fibers through the eventual eyelet in the impregnation tank. Obviously the excess resin removed from the preforming system will have to be collected also in this case in suitable containers, to be subsequently reintroduced into the impregnation tank [11].

- **Heated die**

The heated die is the central part of the pultrusion process. It allows the solidification of the resin, through the curing process, obtaining, at the same time, the right cohesion between resin and fibers. The resin, which enters the mold in the liquid phase, through the supply of heat begins to undergo a gelation process: occurs the so-called cross-linking of the polymer chains, for which the viscous liquid gradually assumes the consistency of a gel, before moving on to the final solid form. Strong adhesion occurs between the gelled resin and wall, whereby it tends to restrict as much as possible the zone in which occurs this stage; adhesive forces that disappear after the vitrification of the resin, with which transformation occurs also shrinkage of the composite section and the consequent detachment from the wall of the mold. This process, which consists in the passage of the resin from the liquid phase to the solid, provides an exothermic reaction, which makes it difficult to control the process (control effected by the speed and temperature control).

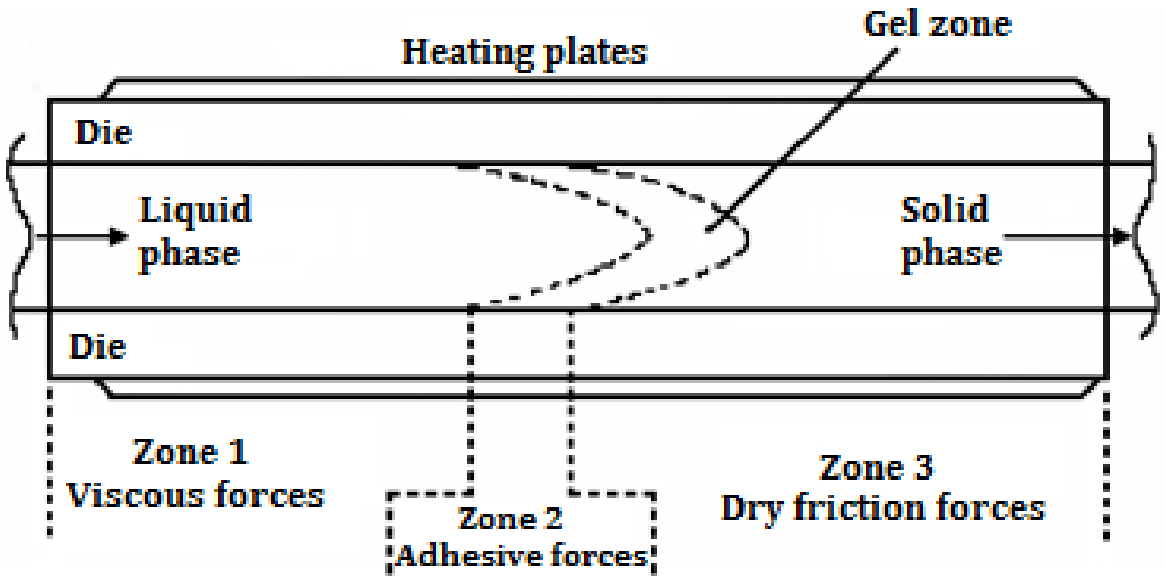

Fig 23: Heating die, [12]

The material used for the die typically consists of a steel alloyed with chromium characterized by a high hardness: the details of the cavity must be able to be machined easily and must resist wear for a high number of cycles (or better, for a high number of meters of pultruded, i.e. the order of tens of thousands); In addition the same cavity is subjected to various surface finishing operations, in order to obtain, at the end of the pultrusion process, a pultruded which does not require additional operations. In order to work the cavity easily, designing multi-piece molds, which fit together to form a hollow having the geometry of the section of the pultruded to realize. By simply adding a spindle trough the cavity of the mold , it is also possible to realize hollow profiles. The heating system may use electric resistors, oil or hot water circulation systems, microwave (the latter is the most recent technique) [11].

- **Pulling system**

There are different pulling systems but the most used are two. The first, most popular, consists in a machine that uses a caterpillar pulling system, which grip and drag the pultruded. The second consists of an alternative clamping machine, consisting of a pair of identical tensioners trucks, which are equipped with special clamps which are activated in an alternating manner: in this way, while the first tensioner block, and drag the pultruded, the other moves with the locking system is deactivated; subsequently, at a given moment, the two tensioning carriages reciprocate, guaranteeing a continuous motion to the pultruded. The clamping and tensioning pull carts are obtained through mechanical or hydraulic transmission mechanisms. There are also some variants, such as the use of two counter-rotating belts, in replacement of the caterpillar pulling system. With the alternative clamping machine it is possible to process any pultruded, as it is sufficient to use locking pliers that they conform to the geometry of the pultruded profile itself, which can also have complex and irregular shapes. Furthermore, with this type of pulling system, in addition to the carriages and to the transmission mechanisms, only two grippers for locking the pultruded are necessary.

The caterpillar system, however, can be used only for simple geometries (none can do caterpillar with geometries that conform to those of the pultruded) or very large geometries. We have, moreover, the need for a very high number of caterpillars, for locking and the pultruded pulling. However, with this shooting system we have the advantage of being able to use a larger clamping length, reducing the local pressure in the gripping of the profile points and lowering, therefore, damage resulting.
Both pulling systems enable the simultaneous production of several lines (which is important to increase the throughput of the production process). However, it is easier to realize a multiple simultaneous production with an alternative clamping system, since, in that case, just add a pair of locking pliers more and to pass the second (third, fourth, ...) pultruded under the same pair of tensioning carriages; in the case of a caterpillar system, on the other hand, to achieve the same multiple production is necessary to add a large number of caterpillars, with consequent expense and more setup times.
Whatever the system adopted, it needs to provide a pull such as to overcome the resistance related to the friction force between the fibers and the mold wall, to viscous forces between the same wall of the mold and the resin not yet solidified and the resistance of the reverse flow of excess resin at the entrance of the mold and in the preforms, as well as that linked to the impregnation system [11].

❖ **Cutting system**

The cutting system generally employs saw as an abrasive disc or even of diamond blades. In some cases it is also used a cooling spray, which, in addition to cool the saw, also minimizes the amount of dust and improves the appearance of the cut pultruded section. The direction of motion of the saw is orthogonal to the motion direction of the pultruded and is, moreover, synchronized with it, so as to obtain the predetermined length of the end piece automatically. After the saw has completed the cutting and has come to the end of the forward stroke, it is returned to the initial position, where it is ready to perform another cut [11].

3.3 Materials

For obtaining a good finished product and for a correct pultrusion process, it is important to keep under control certain parameters, such as the temperature of the mold or the line speed, as well as to choose the most appropriate material quantities. But first it is necessary to choose the most appropriate raw materials to be processed, related to the process demands and to the characteristics required in the market [11].

❖ **Resins**

The characteristics of a resin that can be suitable for the pultrusion must first answer to the application needs. A common feature of all the resins used in composite materials is the low specific weight, while another fairly common feature is the corrosion resistance. Other characteristics such as humidity resistance, electrical insulation or thermal insulation are also quite common, however, they are not always found together in the same resin. Moreover, some

features (such as pigmentation, the lucidity, the surface smoothness or the weather resistance) can be obtained through the use of additives. It is necessary, therefore, to select from time to time, according to specific application requirements, the most suitable resin and the additives to be added in the mixture that will take part in the pultrusion process. Another important factor that affect the choice is the raw material cost. In this regard it follows a first explanation of the low use of thermoplastic resins in the pultrusion process: being very viscous, not easily permeate the fiber even as melted, so as raw material are used it prepregs. To achieve these prepregs, however, there is the need for special processes (prior to pultrusion) that result in higher raw material costs. It follows that the finished products (pultruded) made with the prepreg will have higher costs, which make them difficult to implement. Therefore, only in industries such as aerospace (where cost of the components is not the main key factors) they could be used without distinction. In addition to practical requirements, there are also requirements of processability. In this sense, listed below are the characteristics that a resin must possess and that can most affect the success of the process.

First, a resin for pultrusion should have low initial viscosity, in such a way as to facilitate the impregnation of the fibers, as well as allowing the incorporation of high levels of inorganic filler. This would allow to obtain an economic composition, lower possibility of locking of the mold due to the increased pressurization of the cavity, superior properties in the field of flame retardation and smoke suppression in case of combustion. Without that the viscosity reaches too high levels: acceptable viscosity range from a minimum of 500 cP (for the resins mixed or not with the presence of additional monomer) to a maximum of 800 cP (for resins with additive).

Another feature (together with the low viscosity) that the resin needs so that it fits well in the early stages (bath and preforming) of the pultrusion process is the stability in the liquid phase at room temperature, in such a way as to avoid that it has a premature crosslinking reaction, i.e. away from the mold or even in the pressure tank.

An important feature with respect to the central part of the process is the speed of the cure reaction. In fact it is important that the liquid viscous area inside the mold and the gel-areas are as small as possible, in such a way as to avoid a series of unpleasant phenomena that may lead to breakage of the fibers and / or to the mold block. A small gel-zones would also avoid the aforesaid phenomena at line speeds not too low which this would allow a more cost-efficient production.

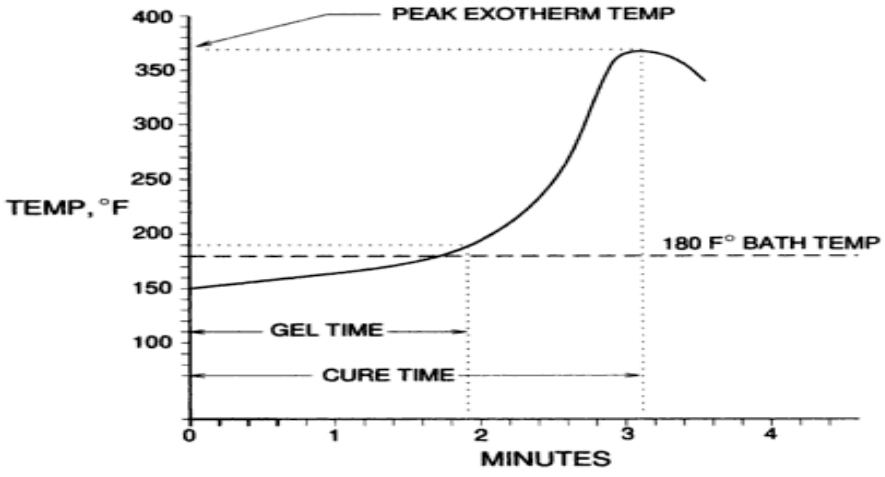

Fig 24: Temperature variation in a cure process, [12]

Based on these considerations and on the database concerning developments of the process in time, it can be said that are good to be pultruded those resins which have a gel time less than 2 minutes, a time interval between the end point of gelation and the point of reaching of the exothermic peak temperature less than one minute, and an exothermic peak temperature between 175°C and 220°C.

As for the applicative and the processability characteristics, it is possible to resort to additional substances with which to mix the resin in order to obtain fundamental properties at the time of processing. Often used, for example, are catalysts which at certain temperatures facilitate the cure reaction, or release agents are used to prevent the resin to adhere to the mold wall and the final pultruded result with an imperfect surface.

Taking into account the mentioned essential features in a pultrusion resin and considering the costs of the raw material, it follows that the (thermosetting) most endeavoured type of resin in this process is the unsaturated polyester resin. By manipulating the relations between acids and glycols it is possible obtain various types of polyester resin, with different levels of reactivity, mechanical or environmental resistance. In general, however, the unsaturated polyester resins have low polymerization times, high tensile strength, a very low cost and, according to the manipulation of acids and glycols, may also possess good chemical and electrical characteristics, depending on the application requirements.

Having a similar chemical, the vinylester resin is the second category of matrices for pultrusion most available on the market. Unlike the polyesters, the vinyl ester have a stronger fiber bond-matrix and result in a composite with improved toughness. Furthermore, they also have a higher corrosion resistance and better properties with regard to thermal distortion than the polyesters. However, they have a slower cure process and higher costs of purchase, so the resulting pultruded part will have a definitely higher cost compared to a polyester resin one. For this reason, the vinylesters are adopted only when specific criteria are required for high-performance applications, which sometimes cannot be reached with polyesters.

A most used variant of vinylester resin is represented by the vinylester with methacrylate, which has a lower viscosity and allows the incorporation of high filler levels, resulting in a more economical composite, with superior properties with regard to flame return and smoke suppression when burning. Furthermore, with this type of resin excellent surface characteristics are obtained, which make they applicable when aesthetics are particularly important.

The epoxy resins are less findable on the pultrusion market, because of their high initial cost and relatively slow reaction rates which result in low process speed. However, it is proper to choose such resins for applications in which better electrical properties in the long term are requests, along with greater mechanical resistance to cutting, better performance in hot / humid environment and higher operating temperatures, since they can quite well withstand up to a maximum of 250°C. The application areas where epoxy resins are most adoperate are aerospace and aeronautics, being especially adopted in combination with carbon fibers or aramid fibers.

With the possibility of providing similar characteristics to epoxy, phenolic resins allow applications at temperatures above 250°C, providing excellent properties in terms of flame spread and smoke generation. These properties make this type of resin suitable for applications where flammable materials are required. However, the high number of pores typically present in final structures of

the phenolic matrix can lead to rather low mechanical properties, and this type of resin is not therefore widely used [7], [11], [12].

❖ **Fibers**

The pultrusion process requires a good degree of orientation of the fibers, in order to obtain a tensile-resistant product. The alignment of the fibers is ensured by means of a pulling system that moves throughout the process. The values of stiffness and axial strength which are obtained by the pultrusion process are much better than those obtainable with other types of manufacturing processes of composite materials.

Most of the pultruded is reinforced with glass roving (characterized by low cost raw material and sufficient mechanical properties). However, when the profile does not require just good axial characteristics, it is essential to use different geometries from simple roving. The roving, in that case, will not be the exclusive reinforcement (but there will still be to ensure the excellent axial properties), but will be joined by a variety of overlapping of reinforcement layers formed from other types of geometries. For example, when the profile to be obtained becomes wider and thinner, it specifically request a larger cross-resistance compared to the more narrow pultruded, where to the layer of roving are added layers of continuous filament mat, which provide a multidirectional increase in mechanical properties. The level of increase of these properties depends on the relative proportions of each reinforcement. Typical pultruded compositions feature of an amount of glass fibers of the 55-60% of the weight, with a ratio roving/mat of 2.5:1. For both roving and mat several varieties of fiber are available, based on the value of their diameter, their distribution and the processing characteristics.

If higher mechanical properties are required, it is possible to use of fabrics, or carbon fibers or aramid fibers may be incorporated inside of the glass fibers. The important thing is not to make too dense this fibrous structures, as this could compromise a good impregnation.

To improve the surface finishing, to obtain a better resistance to weathering, abrasion or corrosion, often there are used surface layers which have the form of webs and that can be made in thermoplastic polyester, in nylon fibers or in fine filaments glass C. These are called the "mat surface", i.e. very light films of about 30 g / m², which are suitable to assume the most complex shapes, unlike the other types of reinforcement. An example of stratification of the various types of reinforcements is shown in figure (Fig 2.6) [12].

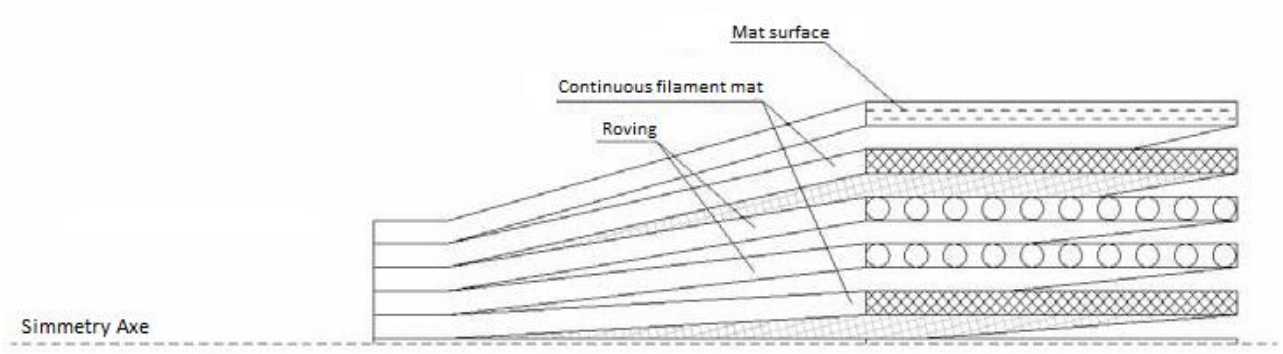

Fig 2.6: Multilayer reinforcement, [12]

3.4 Main issues

A first criticism of the pultrusion process involves the impregnation phase of the fiber in the resin. This step is critical for all composite manufacturing processes, and can be easily obtained by an open bath system. It is just necessary to stretch the fibers by roller and choose a impregnation tank with the right size to allow the resin to occupy every space of what will be the final composite. Compared to other processes, with the pultrusion it is possible to obtain performances above the average, made of good quality composites (without air gaps) and having a high specific volume of fiber. However, there is the problem of the styrene emission, which can be mitigated by proper ventilation. Alternatively it is also possible a variant that allows to completely eliminate emissions of this monomer: it is the pultrusion with online bath.

However in this variant occurs another problem, concerning the difficulties in the impregnation of the densified fiber structure which reaches the mold. In addition there is also a higher cost of equipment. These factors lead to a preference of the classic form of the process, which provides an off-line bathroom like the one described above.

Another factor that is a critical issue for the success of the process and the obtaining of a good finished product is represented by the alignment of the fibers. If the pre-mold step is necessary to stretch the fibers properly and make them go through the preform, in the mold the situation becomes more critical. In fact, comparing the cure of the composite in the mold with thermoplastic extrusion process, it is possible to note a contrast that highlights a number of issues: extrusion thermoplastic resin (unreinforced) passes in molten state the mold, assuming a parabolic velocity profile such that the interface between the resin mold and the speed is zero, while at the center of the cross section it is maximum. Since it is not reinforced resin, this is not a thermoplastic extrusion problem. However, in the case of pultrusion there is resin reinforced and hence a parabolic velocity profile, which may compromise the alignment of the fibers. To avoid this behaviour, it is necessary to pull the fibers axially inside the mold. This operation is not simple. Another solution, more simple and feasible from a practical point of view, is to increase the fraction of the fiber volume, in such a way as to have more fibers that push against the mold surface, forcing the resin to assume a different speed profile from the one parabolic.

Another issue is related to the resin parabolic speed profile, concerning the shear stresses that arise for the velocity gradient in the viscous areas: these efforts are transmitted to the fibers, which in the initial part have not yet completely adhered to the matrix. The breakage of a single fiber can not only lead to a rough surface, but it may even cause a progressive blocking of the mold cavity, which results in the interruption of the process. It is clear that also in this case the tendency to increase the specific volume of fiber greatly alleviate the problems related to the velocity gradient. Moreover, a rapid hardening of the resin (as is generally the case with thermoset resins) may limit the viscous zone and bind together the fibrous structure, preventing breakage of a single fiber.

Another problem which can be solved by increasing the volume of fiber consists in the formation of a cured resin layer on the mold walls (still as a result of the parabolic velocity profile). In fact, if the fiber is not enough to push against the mold walls and to minimize the domain of stationary resin, can easily form a cured resin film on the same walls of the mold, which grows gradually in

thickness, up to the point where the pressure inside the cavity prevents its further growth. At this point, two things can happen: if the cured resin is weak, the fibers periodically cut it, bringing it to the exit of the mold, with a resulting instability of the finished product surface. On the other hand if the hardened resin is strong and is sufficiently linked to the mold walls, the formation of a block within the mold can happen, which results in the interruption of the process and in the need to open the mold to clean it up. Another operation, which helps to eliminate this problem and makes possible the pultrusion process, consists in the introduction of inorganic filler particles inside the resin, so as to achieve a minimum of cavity pressurization which avoids any type of block in the die.

It was shown that many problems can be solved by increasing the amount of fiber in the composite. However it is necessary do not to make the mistake of using fiber volume fractions, greater than a certain threshold (typically 65%) as the matrix performs the task indispensable to distribute the load to the fibers in such a way that the composite does not simply act as a set of unconnected fibers.

For the success of the pultrusion process must still consider other quite critical aspects that do not depend exclusively on the percentage of fiber in the final composition. One of those is the adhesion between resin and wall in the gel-zone. In this area, in fact, the resin-wall adhesion forces are opposed to resin-fiber cohesion forces. This adhesion is even stronger than the one related to the resin stationing in viscous liquid area, which has been discussed previously. To reduce this effect it is necessary to minimize the length of the die segment in which this phenomenon occurs; i.e. it is necessary minimize the length of the gel-areas, doing so as to have a rapid curing process. For this purpose, in addition to use thermosetting resins, a more rapid heat transfer is provided.

It is necessary and important, therefore, to control the temperature of the mold, in order to obtain the desired heat transfer for the realization of the curing process, namely the most critical and the most important phase of the process.

Another parameter that must be kept under control is the line speed, which (as the temperature) has a great influence on the process of cure, and therefore a considerable impact on the chances of success of the pultrusion process. Also it is in a certain way related to temperature: the longer is the initial stretch of the mold in which the temperature is low, the more gel-areas is large (since the cure reaction is exothermic, when the temperature is low the crosslinking is not complete), the lower will be the line speed (to prevent the aforesaid phenomena of breakage of the fibers); vice versa, the more the initial segment of the mold in which the temperature is high (has reached the exothermic peak) temperature is short, the shorter the gel-areas, the higher will be the line speed [10], [12].

3.5 Advantages and limitations

The characteristics of the process that enabled successful applications in many market segments are the great versatility of the most different geometric profiles as well as the design of the different compositions in terms of materials and disposal, the ability to obtain products of unlimited length, the possibility to realize pultruded with high values of the fiber volume, the possibility of obtaining excellent results in terms of fiber alignment (obtaining remarkable axial properties). In addition to that there is the element that probably more than any other has made a difference: the costs of the process. If on the one hand there is a higher initial investment (especially for the realization of the mold), on the other hand there is a low unit cost of the pultruded, made possible by the continuity and the relative automation of the process, in addition to the possibility of working with low cost materials.

An obvious limitation of the pultrusion process consists in the costs too high for working thermoplastic matrices: they, in fact, do not have a viscosity such as to allow easy impregnation of the fiber; for this reason they are used the prepregs, which consist of fibers impregnated with thermoplastic resin previously via special processes. This leads, in fact, to an higher costs of the raw material, involving a too high cost of the finished product.

Another limit is represented by the difficulties of realization of the process form with impregnation in closed mold. This leads to a limitation since the traditional form of the process (which is also the most widespread) involves high styrene emission and therefore the possibility of causing problems for operators.

A limit that regards the pultruded is related to the shape that it can assume: with the pultrusion it is possible to realize only elements with constant cross section. Variable section objects cannot be obtained. At the most, when the section changes are few and not too articulated, it is possible to make changes to the pultruded through subsequent processes, which, of course, will increase the costs of the finished product. This last operation is done quite frequently, since there is needed a certain level of modification or of the pultruded preparation for its correct attachment or for incorporation in a particular finished product.

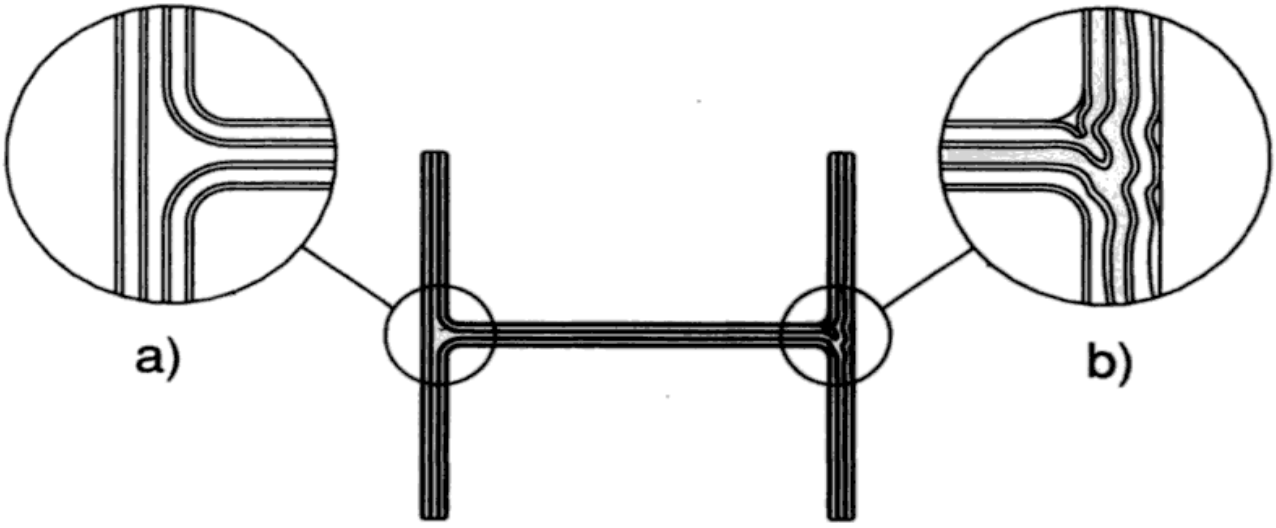

Fig 25: Distribution of the reinforcement layers in a double-T beam, [12]

A final important limitation is the difficulty of obtaining a perfect distribution of the reinforcement layers (mats, fabrics or rovings) into profiles in which there are rounds, with their additional volumes, it is difficult to fill with the same reinforcement. For example, considering the double-T beam represented in figure (Fig 25), it is possible to note how the distribution of the reinforcement layers, which should be the most orderly and symmetrical possible (in order to reduce the anisotropy of the composite) varies according to the point of the section. In fact, in the web and in the flanges of the beam distribution is pretty neat as well as symmetrical. Intersection between web and flanges, vice versa, there is a different positioning of the layers from the expectations.
This problem is caused by the mobility of the impregnated reinforcement, which during the molding process tends to move downward. Moreover at the entrance of the mold there is a considerable hydrostatic pressure, with the return of the resin which causes a local reorganization of the fibers. To mitigate these fibers redistribution phenomena, it is necessary to design accurately the preforming system, ensuring that the resin adheres to the fibers in an optimal manner and that these remain aligned as much as possible. In any case, however, a margin of error always remains and must be taken into account as a component of the pultrusion process [10], [12].

3.6 Pultrusion evolution and applications

The patent of the first pultrusion machine was issued in the US in 1951. Since the middle of 50s begin to find the first manufacturing base of pultruded. Such pultruded had, however, some rather simple geometries and were produced with machines that worked intermittently. Only after the middle of 50s began to spread the first machines for the production of pultruded continuously. This was a first breakthrough, because the continuity of the process allows to achieve higher production volumes: in the early 60s were surveyed 20 companies in the US who based their profit on pultrusion. This number doubled in 1976, after they had a first impulse to the spread of structural shapes in composite: 40 US companies produced about 40 million kilograms of pultruded. This production increased in time (with companies), rising to about 60 million kilograms of 1983. With the advent of the 90 we have a new impetus to the spread of composites, which are starting to be used in a more and more massive in production of assembled parts, in addition to structural parts. It is estimated that in 1994 the pultrusion market in the US was over 90 million kilograms and that a similar amount of pultruded was produced in the rest of the world. In the new millennium, the database acquired in past decades on composite, made possible a continued spread of pultruded in the worldwide market. Currently in the US alone it is estimated to have been put on the market about 250 million kilograms of pultruded every year. Even the rising economic powers of China and India have not been outdone in recent years: in 2006 in China alone have been used about 60 million kilograms of glass as reinforcement for pultruded fiber.
Initially they were pultruded products for sectors such as sports / recreation, in which good mechanical properties are required together with low specific weight values: flagpoles, rods for jump, golf clubs, hockey sticks, sailing mast and fishing rods are some examples of the best known

products. Along with the sports / recreational sector there was a development of the pultrusion in other markets, starting with the electrical, going towards to industrial applications (from the transport sector to the energy sector, the field of anti-corrosion properties).
The characteristics that make the pultrusion process competitive on the market are, first of all, those typical characteristics obtainable by some thermosetting resins combined with glass fiber reinforcement: high strength-to-weight ratio, electrical insulation, corrosion resistance, low coefficient of thermal expansion , thermal insulation. In addition, there are also the characteristics that are unique for pultruded parts, such as the possibility to obtain objects of unlimited length, with an adjustable axial resistance and with the possibility of designing the most diverse sections, with a low cost that is guaranteed by the continuous character of the process [10], [12].

4. Modelling and numerical simulation of curing process

4.1 Introduction

Mathematical modelling aims to describe in mathematical terms the many aspects of the real world and their evolving dynamic. It constitutes the third pillar in science and engineering, in addition to the two most traditional ones which are the theoretical analysis and experimentation.
Simulations are a very powerful numerical analysis tool, used in many scientific and technological fields where there is a difficulty or impossibility to physically reproduce in laboratory the actual conditions to be studied. Numerical modelling and simulation typically makes use of great computing possibilities offered by informatics and processing systems. The simulation therefore can be seen as the transposition, in terms of a logical-mathematical "conceptual model", of the reality. This conceptual or mathematical model can be defined as the set of processes that take place in the system under observation, which together allows to understand the behaviour of the system variables. It is therefore similar to a sort of virtual laboratory that allows a reduction of study costs compared to complex experiments made in real laboratory conditions.
One reason for its growing success is undoubtedly the rapid development of scientific computing, the discipline that allows to translate a mathematical model (solvable in explicit form only in very rare situations) in algorithms that can be treated and resolved by computers. Its use is widespread in the analysis of dynamical systems (simple or complex), either natural (climate system) or artificial (mechanical and automation systems).
There are various methods of numerical analysis. The most used ones for the description of the physical phenomena involved in engineering (including the Finite Element Method used In this work) include the following steps:

- Collection of equations (mostly differential) that describes the physical system;
- Linearization (or simplification) of the model;
- Discretization of the domain (spatial and temporal);
- Selection of an appropriate method of resolution;
- Resolution in the discretized domain;
- Extrapolation to every point of the continuous domain;
- Error analysis.

As it is possible to see from these steps, analytical equations are usually linearized to perform numerical analysis. In addition, the calculation is made on a discretized domain through methods that are often incremental and iterative. This results in an approximate solution, with the certainty of having a certain error in the solution. it is therefore important to be able to find the right compromise between the minimization of the error and the need to have a simple and fast method [8], [13].

4.2 Finite Element Method

The numerical method used in this work is the Finite Element Method (FEM). This is a numerical technique for calculating approximate solutions of problems described by partial differential equation, reducing them to a system of algebraic equations. In general, the Finite Element Method is well suited to solve partial differential equations when the domain has complex shape (such as the chassis of a car or an aircraft engine), when the domain is variable (for example, a solid state reaction with variable boundary conditions), when the required accuracy to the solution is not homogeneous on the domain (in a crash test on a motor vehicle, the required accuracy is greater in the vicinity of the impact area) and when the solution lacks regularity.
The FEM can be applied to physical bodies that are divisible into a number of elements of defined shape and dimensions. In the continuum, each finite element is considered a numerical integration field of homogeneous characteristics.
The main feature of the Finite Element Method is the discretization process, where a grid (mesh) is made up of primitives (finite element) in coded form (triangles and quadrilaterals in 2D domains, hexahedrons and tetrahedrons for 3D domains). On each element characterized by this basic form, the solution of the problem is assumed to be expressed by a linear combination of lagrangian functions, called “basis functions” or “shape functions”. Sometimes the functions are approximated, and those calculated in the integration points not necessarily will be the exact values of the function, but instead the values that provide the least error on the entire solution. The more the grid is refined, the lower should be the error (in the numerical stability limits).

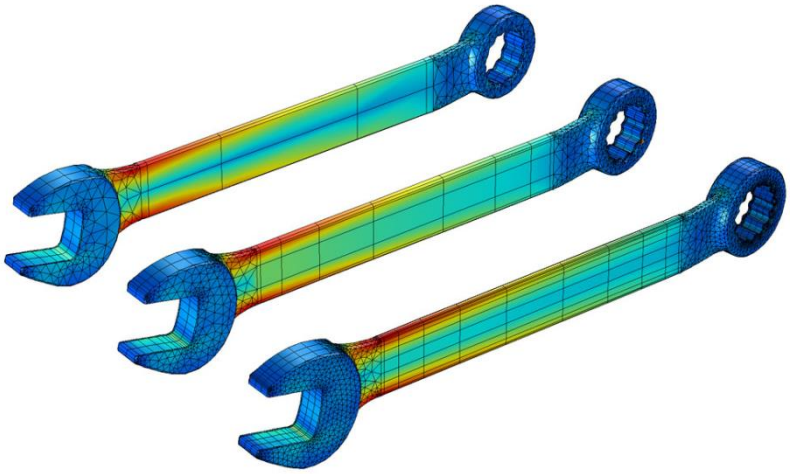

Fig 26: Examples of FEM results, [8]

In its most common form, the Finite Element Method is used to solve the problems described by linear constitutive laws: usually the stress-deformations problems in the elastic range or the heat diffusion inside a material body. Some more sophisticated solutions allow to explore the behaviour of the materials even in highly non-linear range, assuming plastic or viscoplastic behaviour, for instance, sometimes coupled problems are also treated, within which it is possible to solve simultaneously several complementary aspects related to different analysis. For instance, the problem of the geotechnical behaviour of a soil (geomechanical field) in the presence of groundwater seepage (hydrogeological field).

The approximate algebraic equations are different depending on the type of problem, the type of item and the approximation type (linear or polynomial) to be obtained. In this work, a thermomechanical problem was proposed to be solved, by means of eight nodes hexahedral isoparametric elements and the use of programming capabilities of ABAQUS FEM software [8], [13].

4.3 Overview of ABAQUS software

ABAQUS is the software suite for finite element analysis (FEA) and computer-aided engineering used in this work. The Abaqus FEA product suite offers powerful and complete solutions for complex design problems and routine, covering a wide spectrum of industrial applications. In the automotive sector, the design work groups are able to consider the full load of the vehicle, the dynamic vibration, the multibody systems, impact / collision, the nonlinear static coupling, the thermal coupling and the acoustic / structural coupling using a common model data structure and integrated solver technology. The cutting-edge companies benefit from the Abaqus FEA suite to consolidate their processes and tools, reduce costs and inefficiencies, and gain a competitive advantage. Abaqus was initially designed to address non-linear physical behaviour and as a result, the package has an extensive range of material models.

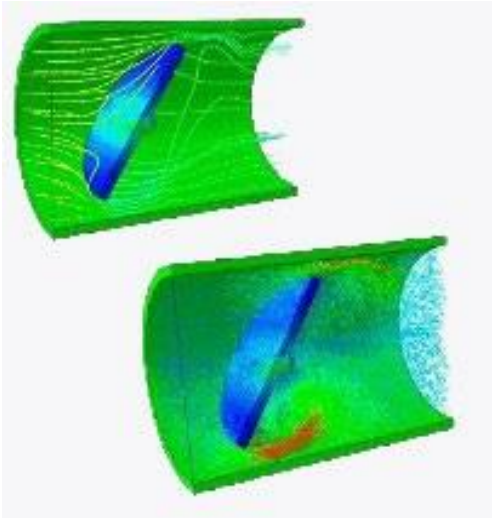

Fig 27: Abaqus simulation of the air flow in intake engine manifold, [10]

The Abaqus suite consists of four core products: Abaqus/Standard, Abaqus/Explicit, Abaqus/CFD and Abaqus/CAE (Complete Abaqus Environment).

Abaqus/Standard employs solution technology ideal for static and low-speed dynamic events, where highly accurate stress solutions are critically important.

Abaqus/Explicit is a finite element analysis product that is particularly well-suited to simulate brief transient dynamic events such as consumer electronics drop testing, automotive crashworthiness and ballistic impact.

Abaqus/CFD provides advanced computational fluid dynamics capabilities with extensive support for pre-processing and post processing provided in Abaqus/CAE. These scalable parallel CFD

simulation capabilities address a broad range of nonlinear coupled fluid-thermal and fluid-structural problems.

With Abaqus/CAE it is possible to quickly and efficiently create, edit, monitor, diagnose, and visualize advanced Abaqus analyses. An intuitive interface integrates modelling, analysis, job management and results visualization in a consistent, easy-to-use environment.

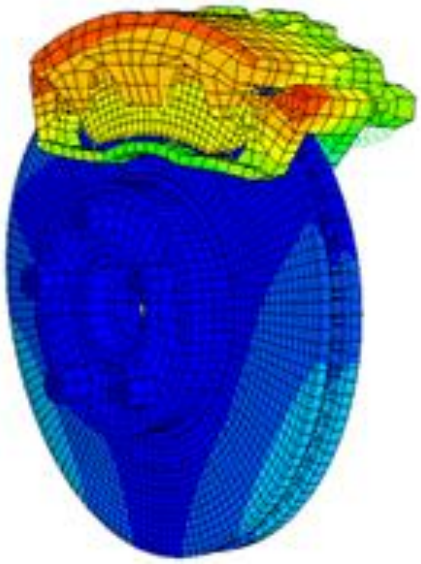

Fig 28: Abaqus simulation of the stresses on a brake calliper, [9]

4.4 Overview of the ABAQUS subroutines developed for this work

Abaqus allows using some Fortran subroutine in order to increase the potential of the software, letting the user change the usual calculations. The phenomena occurring in real systems are always much more complex than one can or wants to simulate. In the default version of the software, the routines for calculating just simulate a narrow range of phenomena considered fundamental.
It is necessary therefore to use subroutines whenever there is the interest in simulating complex behaviours or use innovative elements or access variables not found among the various output that default Abaqus provides by default. Abaqus in the latest version provides 85 user subroutine applicable in the various environments (standard, explicit, CFD) with many different purposes.
Listed below are the subroutines created specifically for this work [14].

- **UEXTERNALDB:** In this work, this user subroutine is used for reading from an external file the connectivity matrix, the nodes position and the degree of cure, and for writing on file the updated degree of cure. It is called once each at the beginning of the analysis, at the beginning of each increment, at the end of each increment, and at the end of the analysis. It makes available a variable (called LOP) that indicates in which phase of the analysis the subroutine is called;
- **HETVAL:** It is used to define a heat flux due to internal heat generation in a material, for example, as might be associated with phase changes occurring during the solution. This subroutine allows for the dependence of internal heat generation on state variables (such as the fraction of transformed material) that themselves evolve with the solution and are stored as solution dependent state variables. In this work it is used for simulating the heat generation that occur during the exothermic curing process;
- **USDFLD:** This subroutine can be used to introduce a solution dependent material property field since such properties can easily be defined as functions of field variables. It allows to define field variables at a material point as functions of any of the available material point quantities. In this user subroutine there is the core of this work, where each increment it defines the value of the degree of cure;
- **UMAT:** This subroutine is used to define the mechanical constitutive behaviour of a material. It must update the stresses and solution dependent state variables to their values at the end of the increment for which it is called. It must provide the material Jacobian matrix $\partial\Delta\sigma/\partial\Delta\varepsilon$ for the mechanical constitutive model;
- **UEXPAN:** This user subroutine is called for models in which the thermal strains depend on temperature and/or predefined field variables in complex ways or depend on state variables, which can be used and updated in this routine. In this work it is used for the simulation of the volume variation of the composite due to the thermal expansion and the chemical shrinkage strain.

4.5 Mathematical model

In this work it is proposed to simulate the phenomena that occur during the polymerization of the resin in pultrusion process. The cure takes place during the passage into the die and in the immediate aftermath. The purpose was therefore to simulate in every point of the composite the degree of cure, the temperature, heat generation, the state of stress-strain. It is therefore clear that it is a problem that involves chemical, thermodynamic and mechanical phenomena and all of them are related each other.

The thermodynamic model is based on the heat equation. The heat equations wrote for the die and for the composite assume different forms due to the different characteristics of materials. The die is an isotropic conductor steel so its behaviour is very simple to describe. The composite is an orthotropic body with respect to the frame of reference chosen (axes parallel to the mold dimensions with z axis parallel to the pulling direction as shown in Fig 29). in particular it is transversely isotropic then it is possible to distinguish two different behaviours: longitudinal and transversal. The composite is also characterized by an internal heat generation related to the degree of cure of the resin.

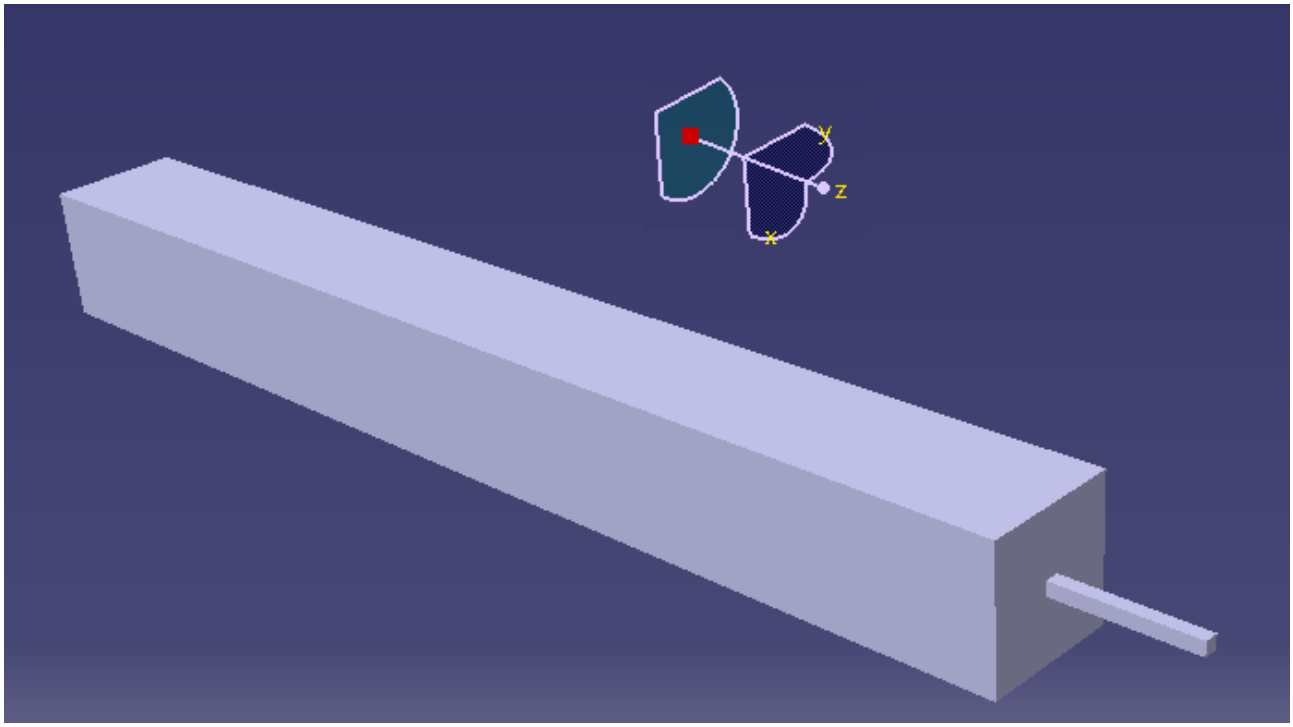

Fig 29: Catia CAD model of dies and composite profile

It follows the thermochemical model proposed in many previous works ([1],[2],[3]) and used for the present. The heat equation wrote for the composite and the die are the following:

$$(\rho C_p)_c \left(\frac{\partial T}{\partial t} + u\frac{\partial T}{\partial z}\right) = K_{L,c}\frac{\partial^2 T}{\partial z^2} + K_{T,c}\frac{\partial^2 T}{\partial x^2} + K_{T,c}\frac{\partial^2 T}{\partial y^2} + q \tag{23}$$

$$(\rho C_p)_c \frac{\partial T}{\partial t} = K_d\frac{\partial^2 T}{\partial z^2} + K_d\frac{\partial^2 T}{\partial x^2} + K_d\frac{\partial^2 T}{\partial y^2} \tag{24}$$

where the subscript *c* and *d* means respectively "composite" and "die", ρ is the density, C_p is the specific heat at constant pressure, T is the temperature, t is the time, u is the speed in pulling direction, $K_{L,c}$ and $K_{T,c}$ are the composite thermal conductivities in the longitudinal and transversal direction, K_d is the die thermal conductivity. In the composite heat equation there is also a source term q related to the heat generation and due to the exothermic behaviour of the cure reaction:

$$q = \left(1 - V_f\right)\rho_r H_{tr} R_r(\alpha, T) \tag{25}$$

In this equation V_f is the fiber volume ratio, ρ_r is the density of the resin, H_{tr} is the total heat amount produced during the complete reaction, $R_r(\alpha, T)$ is the rate of resin reaction and is function of temperature and degree of cure α, and it is usually assumed equal to the time derivative of the degree of cure.

In this work it has been used a model built for epoxy resin, represented by an Arrhenius-type equation:

$$R_r(\alpha, T) = A_0 exp\left(\frac{-E_a}{R\,T}\right)(1 - \alpha)^n. \tag{26}$$

By means a translation of the derivative of the degree of cure in an Eulerian frame of reference, it results the following relation:

$$R_r(\alpha, T) = \frac{d\alpha}{dt} = \frac{\partial \alpha}{\partial t} + \frac{\partial \alpha}{\partial z}\frac{dz}{dt} = \frac{\partial \alpha}{\partial t} + u\frac{\partial \alpha}{\partial z}. \tag{27}$$

Operating some easy algebraic passages, it follows that:

$$\frac{\partial \alpha}{\partial t} = R_r(\alpha, T) - u\frac{\partial \alpha}{\partial z} \tag{28}$$

and since the phenomenon is assumed stationary, the partial derivative is null:

$$R_r(\alpha, T) = u\frac{\partial \alpha}{\partial z}. \tag{29}$$

Ultimately the thermochemical problem on the composite parts can be summarised in the following system:

$$\begin{cases} \left(\rho C_p\right)_c\left(\dfrac{\partial T}{\partial t} + u\dfrac{\partial T}{\partial z}\right) = K_{L,c}\dfrac{\partial^2 T}{\partial z^2} + K_{T,c}\dfrac{\partial^2 T}{\partial x^2} + K_{T,c}\dfrac{\partial^2 T}{\partial y^2} + \left(1 - V_f\right)\rho_r H_{tr} A_0 exp\left(\dfrac{-E_a}{R\,T}\right)(1 - \alpha)^n \\ A_0 exp\left(\dfrac{-E_a}{R\,T}\right)(1 - \alpha)^n = u\dfrac{\partial \alpha}{\partial z} \end{cases} \tag{30}$$

The curing process of the resin significantly influences also the mechanical properties of the composite. In this work it has been followed the approach proposed by Bogetti and Gillespie [4].

They proposed a simplified version of the Cure Hardening Instantaneous Linear Elastic (CHILE) approach. It is shown in the following relation:

$$E_r = \begin{cases} E_0\,, & T^* \le T_{C1} \\ E_0 + \frac{T^* - T_{c1}}{T_{c2} - T_{c1}}\left(E_\infty - E_0\right), & T_{C1} < T^* \le T_{C2} \\ E_\infty\,, & T_{C2} < T^* \end{cases}, \tag{31}$$

where E_0 and E_∞ are, respectively, the totally uncured and the totally cured resin Young moduli, T_{c1} and T_{c2} are the critical temperatures of starting and ending of the glass transition, and T^* is a temperature that can be expressed as:

$$T^* = T_g - T, \tag{32}$$

where T is the temperature of the resin and T_g is the instantaneous glass transition temperature. Experimental results show that the temperature T_g is function of the degree of cure α, and its behaviour can be simplified by means a linear function:

$$T_g = T_{g0} + B\alpha, \tag{33}$$

where T_{g0} represents the instantaneous glass transition temperature of the uncured resin and B is a constant parameter of the resin.
The complete CHILE model is plotted in Fig 3.5.

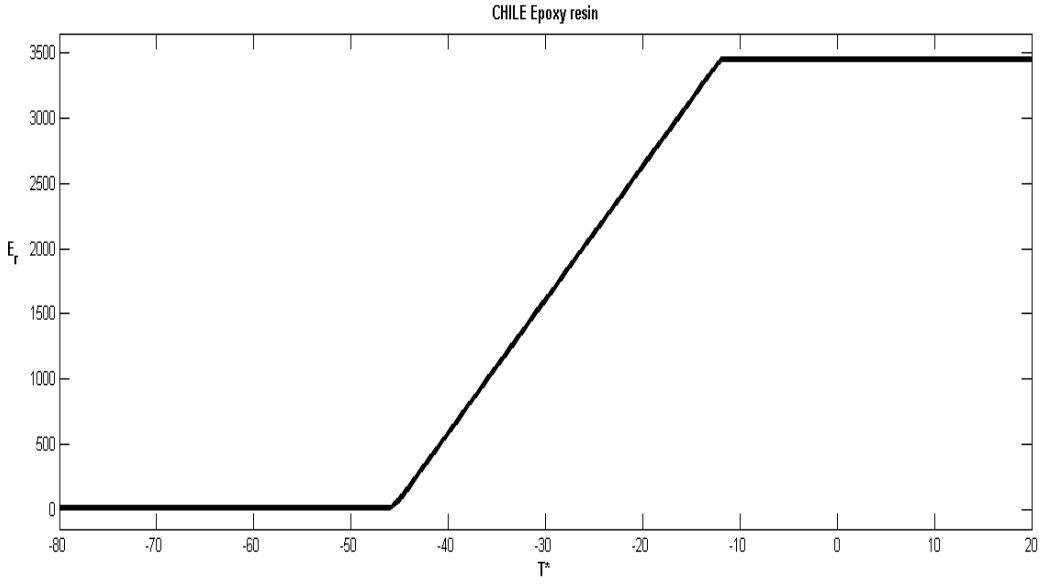

Fig 30: CHILE model graphical representation

To fully describe the mechanical properties of the resin, it must also be defined the shear modulus G_r and Poisson's ratio ν_r . Since the resin pass from a liquid state of aggregation to a glassy state, the Poisson's ratio has been assumed as a linear function of the degree of cure α, with varies from 0.5 (Poisson's ratio of the incompressible liquids) to 0.35 (Poisson's ratio of the glassy epoxy resin):

$$\nu_r = 0.5 - \alpha(0.5 - 0.35). \tag{34}$$

The shear modulus $G_r$can be found by means the following relation:

$$G_r = \frac{E_r}{2(1+\nu_r)}. \tag{35}$$

Since all the characteristic of the resin has been described it is possible to compute the mechanical characteristic of the composite. It will be followed again the approach proposed by Bogetti and Gillespie [5]. The composite material is composed of an epoxy resin matrix (isotropic) and of unidirectional glass fiber rovings (transversally isotropic). So the composite material can be also considered transversally isotropic.

In the following equations the subscripts "f" and "r" mean that the variable refers respectively to fiber and resin, the subscript "L" means longitudinal and the subscript "T" means transversal. The variable without subscripts "f" or "r" refers to the composite.
The longitudinal Young modulus of the composite is:

$$E_L = E_{L,f}V_f + E_r(1 - V_f) + \left(\frac{4(\nu_r - \nu_{LT,f})k_f k_r(1-V_f)V_f}{(k_f+G_r)k_r+(k_f-k_r)G_r V_f}\right); \tag{36}$$

where k_f and k_r are the isotropic bulk moduli for fiber and resin:

$$k_f = \frac{E_{L,f}}{2\left(1-\nu_{LT,f}-2\nu_{LT,f}^2\right)}, \tag{37}$$

$$k_r = \frac{E_r}{2(1-\nu_r-2\nu_r^2)}. \tag{38}$$

The transverse Young modulus of the composite is:

$$E_T = \frac{1}{(4k_t)^{-1}+(4G_{TT})^{-1}+\left(\nu_{LT}^2/E_L\right)}, \tag{39}$$

where k_t is the effective plane strain bulk modulus:

$$k_t = \frac{(k_f+G_r)k_r+(k_f-k_r)G_r V_f}{(k_f+G_r)-(k_f-k_r)V_f}. \tag{40}$$

The shear moduli of the composite are:

$$G_{LT} = G_r\left(\frac{(G_{LT,f}+G_r)+(G_{LT,f}-G_r)V_f}{(G_{LT,f}+G_r)-(G_{LT,f}-G_r)V_f}\right), \tag{41}$$

$$G_{TT} = \frac{G_r\left(k_r(G_r+G_{TT,f})+2G_{TT,f}G_r+k_r(G_{TT,f}-G_r)V_f\right)}{k_r(G_r+G_{TT,f})+2G_{TT,f}G_r-(k_r+2G_r)(G_{TT,f}-G_r)V_f}, \tag{42}$$

where the shear modulus of the fiber is:

$$G_{TT,f} = \frac{E_{T,f}}{2(1+\nu_{TT,f})}. \tag{42}$$

The Poisson's ratios of the composite are:

$$\nu_{LT} = \nu_{LT,f}V_f + \nu_r(1 - V_f)\left(\frac{(\nu_r-\nu_{LT,f})(k_r-k_f)G_r(1-V_f)V_f}{(k_f+G_r)k_r+(k_f-k_r)G_r V_f}\right), \tag{43}$$

$$\nu_{TT} = \frac{2E_L k_t - E_L E_T - 4\nu_{LT}^2 k_t E_t}{2E_L k_t}. \tag{44}$$

With the mechanical properties as shown before it is possible to build the material Jacobian matrix. For this problem all the normal stresses and one of the shear stress (τ_{LT}) will be computed. It results in the following relation:

$$\underline{\sigma}^{mech} = \underline{\underline{J}} * \underline{\varepsilon}^{mech} \Rightarrow \begin{bmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \\ \tau_{zx} \end{bmatrix} = \begin{bmatrix} \frac{1-\nu_{LT}^2}{E_L E_T \Delta} & \frac{\nu_{TT}+\nu_{LT}^2}{E_L E_T \Delta} & \frac{\nu_{LT}+\nu_{LT}\nu_{TT}}{E_L E_T \Delta} & 0 \\ \frac{\nu_{TT}+\nu_{LT}^2}{E_L E_T \Delta} & \frac{1-\nu_{LT}^2}{E_L E_T \Delta} & \frac{\nu_{LT}+\nu_{LT}\nu_{TT}}{E_L E_T \Delta} & 0 \\ \frac{\nu_{LT}+\nu_{LT}\nu_{TT}}{E_T^2 \Delta} & \frac{\nu_{LT}+\nu_{LT}\nu_{TT}}{E_T^2 \Delta} & \frac{1-\nu_{TT}^2}{E_T^2 \Delta} & 0 \\ 0 & 0 & 0 & 2G_{LT} \end{bmatrix} * \begin{bmatrix} \varepsilon_x \\ \varepsilon_y \\ \varepsilon_z \\ \gamma_{zx} \end{bmatrix}, \tag{46}$$

where the value Δ is:

$$\Delta = \frac{1-2\nu_{LT}^2-\nu_{TT}-2\nu_{LT}^2\nu_{TT}}{E_T^2 E_L}. \tag{47}$$

The total strain is calculated by adding to the mechanical deformation the thermal and the chemical strains. Even in thermal expansion the composite behave as transversely isotropic. Therefore are defined two different coefficients of thermal expansion are defined:

$$CTE_L = \frac{CTE_{L,f}E_{L,f}V_f + CTE_r E_r(1-V_f)}{E_{L,f}V_f + E_r(1-V_f)}, \tag{48}$$

$$CTE_T = \left(CTE_{T,f} + \nu_{LT,f}CTE_{L,f}\right)V_f + (CTE_r + \nu_r CTE_r)(1-V_f) - \left(\nu_{LT,f}V_f + \nu_r(1-V_f)\right)CTE_L. \tag{49}$$

Each component ε_i^{th} of the thermal strain array is given by:

$$\varepsilon_i^{th} = CTE_i * \Delta T. \tag{50}$$

The chemical strain is due to the shrinkage of the resin during the cure process. The chemical strain of the resin is modelled by the following equation:

$$\varepsilon_r = \sqrt[3]{1+\Delta V_r} - 1, \tag{51}$$

where ΔV_r, the incremental specific volume shrinkage of the resin, is function of the degree of cure and of the total volumetric shrinkage V_{sh}:

$$\Delta V_r = \Delta\alpha * V_{sh}. \tag{51}$$

For the composite material, it results the following chemical strains:

$$\varepsilon_L^{ch} = \frac{\varepsilon_r E_r(1-V_f)}{E_{L,f}V_f + E_r(1-V_f)}, \tag{53}$$

$$\varepsilon_T^{ch} = (\varepsilon_r + \nu_r\varepsilon_r)(1-V_f) - \left(\nu_{LT,f}V_f + \nu_r(1-V_f)\right)\varepsilon_L^{ch}. \tag{54}$$

4.6 ABAQUS problem setting

The problem has been set on the ABAQUS graphic interface. It was built the geometry of the di and the composite profile. The geometry is only representative of one quarter of the real system. Thanks to the symmetry conditions, covered later, it is possible to expand the results to the entire real system (Fig 31).
The system is composed of a steel die 100 x 100 x 900 mm, drilled in the center of the cross section by a square hole 10 x 10 mm having dimensions parallel to the lateral faces of the mold.
The characteristics of the materials are shown in the following passage of the .inp file.

```
** MATERIALS
**
*Material, name=Composite
*Conductivity, type=ORTHO
 0.000559, 0.000559, 0.000905
*Density
 2.0907e-06,
*Depvar
     1444,
*Expansion, type=ORTHO, user
*Heat Generation
*Specific Heat
 797.27,
*User Defined Field
*User Material, constants=1
0.,
*Material, name=Steel
*Conductivity
 0.04,
*Density
 7.833e-06,
*Elastic
210000., 0.3
*Specific Heat
460.,
```

In this passage of the .inp file the characteristic of the material required by ABAQUS for the simulation are reported. The lines staring with double star "**" are comments, the lines starting with the single star "*" are command lines and the lines without stars are value assignments related to the command in the previous line. The first material presented is the composite one. It is an orthotropic material therefore three values of conductivity are required. Since the profile (the part modelled in composite material) is transversally isotropic the values along the dimensions *x* and *y* are the same, while the value along *z* axis (longitudinal dimension). The values of conductivity are reported in W/(mm*K). The density is reported in Kg/mm^3. DEPVAR is the number of state variables defined for this material. Specific heat is defined in J/(Kg*K). The commands Expansion, Heat Generations, User Defined Field and User Material call the subroutines later described.
The Steel material contains the characteristics of the die. Its definition is much easier than the one of composite, since the die is assumed isotropic and the standard ABAQUS tools were used for its modelling. The elastic command require the Young's module (expressed in N/mm^2) and the Poisson's ratio.

It is possible to see that the program, for the composite material, call some subroutines that will be shown in details in the next paragraph. The "*Expansion" command call the UEXPAN user subroutine in which is simulated the chemical and thermic strain, the "*Heat Generation" command call the HETVAL subroutine in which is modelled the heat generation due to the exothermic cure process; the "*User Defined Field" command call the USDFLD subroutine that has the task to compute the value of the degree of cure in each point of the composite; the "*User

Material" command call the UMAT subroutine in which are modelled the mechanical characteristic of the composite profile by means his Jacobian matrix and in which is computed the stress array in each element.

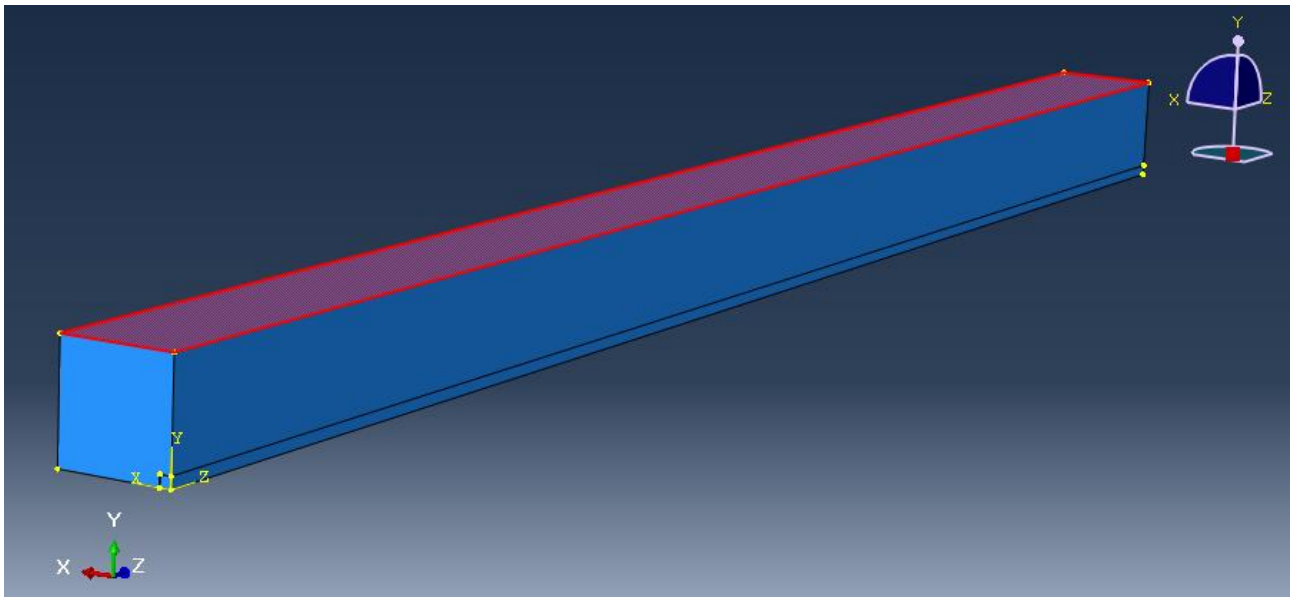

Fig 31: Abaqus geometry

ABAQUS allows to simulate the interaction between the two parts involved in the problem. In this work it has been simulated a thermic and mechanic simulation. The thermic contact simulates the conduction between the parts, the mechanic contact in this problem just simulates the no penetration condition. It has been simulated also the natural convection between the exposed faces of the die and the environment, which is set at 293 K. The effect of the heaters has been simulated by means of an imposed temperature of 423 K on the top face of the die (red surface in Fig 31). It has been imposed the temperature of the composite in the entrance section equal to the environmental temperature (493 K). The symmetry conditions are both mechanical and thermic (i.e., mechanical constrains and adiabaticity on the symmetry faces). The pulling force has been simulated by means of a tensile pressure on the composite profile.

4.7 ABAQUS subroutines developed

The phenomena occurring within the mold of a pultrusion system are not only mouldable using the tools provided in the ABAQUS graphics interface. It is necessary then, as already explained previously, to use some subroutines provided by ABAQUS.
Subroutines, written in Fortran language, have the purpose of extend the power of software allowing the user to build custom templates that are better reconciled to the problem analysed.
It follow the code of the subroutines used in this work.

```
      SUBROUTINE UEXTERNALDB(LOP,LRESTART,TIME,DTIME,KSTEP,KINC)

      INCLUDE 'ABA_PARAM.INC'
C

      real,dimension(1444) :: STATEV
      DIMENSION TIME(2)

C
      call GETVRM ('STATEV',ARRAY,JARRAY,FLGRAY,JRCD,JMAC,JMATYP,
     1 MATLAYO,LACCFLA)
      STATEV=ARRAY

      if ((LOP.eq.0).or.(LOP.eq.1).or.(LOP.eq.4)) then
C Readings
          call read_data(STATEV)
      else
C Writings
          call write_data(STATEV)

      end if

      RETURN
      END
```

The UEXTERNALDB subroutine is called once each at the beginning of the analysis, at the beginning of each increment, at the end of each increment, and at the end of the analysis. The command GETVRM allow to call ABAQUS variables not defined within subroutine's default variables passed in for information. In this subroutine STATEV (an array containing the solution-dependent state variables) is called. The LOP variable can assume values within the interval [0:4] that indicates in which part of the analysis the subroutine is called. In particular if LOP has value 0, 1 or 4 (if the subroutine is called respectively at start of the analysis, at the start of the current analysis increment or at the beginning of a restart analysis) the program require to read data from external files, therefore it calls the "read_data" subroutine. Otherwise, if LOP assumes the value 2 or 3 (if the subroutine is called respectively at the end of the current analysis increment or at the end of the analysis) the program must update the values of the cure on an external file therefore it calls the "write_data" subroutine.

```
      SUBROUTINE HETVAL(CMNAME,TEMP,TIME,DTIME,STATEV,FLUX,
     1 PREDEF,DPRED)
C
      INCLUDE 'ABA_PARAM.INC'
C
```

```
      CHARACTER*80 CMNAME
C
      DIMENSION TEMP(2),STATEV(*),PREDEF(*),TIME(2),FLUX(2),
     1 DPRED(*)
      real:: alpha,Vf,rho,Htr,A0,Ea,R,n,nn

      STATEV(1)=TEMP(1)
      nn=STATEV(4)+4
      alpha=STATEV(nn)
      Vf=0.6
      rho=1260.0
      Htr=324.0
      A0=192000.0
      Ea=60.0
      R=0.008314
      n=1.69
      FLUX(1)=rho*(1-Vf)*Htr*A0*(EXP(-Ea/(R*TEMP(1))))*((1-alpha)**n)
      FLUX(2)=rho*(1-Vf)*Htr*A0**Ea/(R*TEMP(1)**2)*(EXP(-Ea/(R*TEMP(1)))
     1 )*((1-alpha)**n)


      RETURN
      END
```

The HETVAL subroutine is used to define a heat flux due to the internal heat generation described by equation (25). The main purpose of this subroutine is to define the array FLUX. In the first position (FLUX(1)) of this array heat flux in the current material calculation point is reported. In the second position (FLUX(2)) the rate of change of heat flux per temperature , $\frac{\partial q}{\partial T}$, is reported.

```
      SUBROUTINE USDFLD(FIELD,STATEV,PNEWDT,DIRECT,T,CELENT,
     1 TIME,DTIME,CMNAME,ORNAME,NFIELD,NSTATV,NOEL,NPT,LAYER,
     2 KSPT,KSTEP,KINC,NDI,NSHR,COORD,JMAC,JMATYP,MATLAYO,LACCFLA)
C
      INCLUDE 'ABA_PARAM.INC'
C
      CHARACTER*30 file1
      CHARACTER*80 CMNAME,ORNAME
      CHARACTER*3  FLGRAY(15)
      DIMENSION FIELD(NFIELD),STATEV(NSTATV),DIRECT(3,3),
     1 T(3,3),TIME(2)
      DIMENSION ARRAY(15),JARRAY(15),JMAC(*),JMATYP(*),COORD(*)
      real, dimension (1,1440) :: cure
      real, dimension (9) :: vect
      real, dimension (1440,9) :: Element
      real, dimension (8) :: nn, x
      real, dimension (2275,4) :: Node
      real, dimension (2) :: tem
      real:: f,df,dx,alpha,alpha_p,Ea,R,u,n,Temper,A0,ind,num_el


      alpha_p=ARRAY(1)
      Temper=STATEV(1)
      A0=192000.0
      Ea=60.0
      R=0.008314
      n=1.69
      u=15   !900 mm/min
C Finding previous element
      dx=100.0
      file1="C:\Users\Fausto\Desktop\Fausto\Connectivity.txt"
```

```
      open (unit=1, file=file1)
      do i=1, num_el
          read (1,*) vect
          do j=1,9
              Element(i,j)=vect(j)
          end do
      end do
      close (1)
      nn(1)=Element(NOEL,2)
      nn(2)=Element(NOEL,3)
      nn(3)=Element(NOEL,4)
      nn(4)=Element(NOEL,5)
      nn(5)=Element(NOEL,6)
      nn(6)=Element(NOEL,7)
      nn(7)=Element(NOEL,8)
      nn(8)=Element(NOEL,9)
      file1="C:\Users\Fausto\Desktop\Fausto\coord_nodes.txt"
      open (unit = 1, file=file1)
      do i=1, num_el
          read (1,*) vect
          do j=1,9
              Node(i,j)=vect(j)
          end do
      end do
      close (1)
      x(1)=Node(nn(1),4)
      x(2)=Node(nn(2),4)
      x(3)=Node(nn(3),4)
      x(4)=Node(nn(4),4)
      x(5)=Node(nn(5),4)
      x(6)=Node(nn(6),4)
      x(7)=Node(nn(7),4)
      x(8)=Node(nn(8),4)

      if ((x(1).eq.0).or.(x(2).eq.0).or.(x(3).eq.0).or.(x(4).eq.0)
     1.or.(x(5).eq.0).or.(x(6).eq.0).or.(x(7).eq.0).or.(x(8).eq.0)) then
C Initial element
          alpha_p=0
          dx=dx/2
      else
C Generic element
C Find the smaller x
          do i=1, 7
              do j=i+1, 8
                  if (x(j)<x(i)) then
                      tem(1)=nn(j)
                      tem(2)=x(j)
                      nn(j)=nn(i)
                      x(j)=x(i)
                      nn(i)=tem(1)
                      x(i)=tem(2)
                  end if
              end do
          end do

C Finding adjacent element
          do i=1, num_el
              do j=2, 9
                  if (Element(i,j)==nn(1)) then
                      do k=2, 9
                          if (Element(i,k)==nn(2)) then
                              do jj=2, 9
                                  if (Element(i,jj)==nn(3)) then
```

```
                                    El_prec=Element(i,1)
                                end if
                            end do
                        end if
                    end do
                end if
            end do
        end do
C Reading on file Cura.txt the value of the degree of cure in the adjacent element
C If it is not present use the standard value
        if (cure(1,El_prec)==-1) then
            if (COORD(3)<200) then
                alpha_p=0
                dx=COORD(3)
            else if (COORD(3)<400) then
                alpha_p=0.03
                dx=COORD(3)-200
            else if (COORD(3)<600) then
                alpha_p=0.15
                dx=COORD(3)-400
            else if (COORD(3)<800) then
                alpha_p=0.45
                dx=COORD(3)-600
            else
                alpha_p=0.82
                dx=COORD(3)-800
            end if
        end if
      end if
      STATEV(2)=dx
      STATEV(4)=NOEL

c     Newton-Rapson: Initial attempt alpha=alpha_p
      alpha=alpha_p
      eps=0.001
      er=1

      do while (er>eps)
          f=u*(alpha-alpha_p)/dx-A0*(EXP(-Ea/(R*Temper)))*
     1    ((1-alpha)**n)
          df=u/dx-A0*(EXP(-Ea/(R*Temper)))*((1-alpha)**(n-1))*n
          alpha_new=alpha-f/df
          er=abs(alpha-alpha_new)
      end do
      FIELD=alpha
      ind=NOEL+4
      STATEV(ind)=alpha

      RETURN
      END
```

The USDFLD subroutine is used to define the values of the degree of cure at a material point as functions of temperature (as it was described in paragraph 4.5). In this case it has also the task to find the value of the degree of cure of the adjacent element that precedes, in longitudinal (*z*) direction, the one in which computation is going on. It has been taken into account also the possibility that the computation is going on in the first cross-section of the profile. In this case it is considered that the value of the degree of cure in the entry section is null (boundary condition). A Newton-Rapson iterative method has been developed in aim to find the degree of cure value. The

final result is saved in the FIELD variable, as required by the default subroutine, and in the STATEV array in the position relative to the element.

```
      SUBROUTINE UMAT(STRESS,STATEV,DDSDDE,SSE,SPD,SCD,
     1 RPL,DDSDDT,DRPLDE,DRPLDT,
     2 STRAN,DSTRAN,TIME,DTIME,TEMP,DTEMP,PREDEF,DPRED,CMNAME,
     3 NDI,NSHR,NTENS,NSTATV,PROPS,NPROPS,COORDS,DROT,PNEWDT,
     4 CELENT,DFGRD0,DFGRD1,NOEL,NPT,LAYER,KSPT,JSTEP,KINC)
C
      INCLUDE 'ABA_PARAM.INC'
C
      CHARACTER*80 CMNAME
      DIMENSION STRESS(NTENS),STATEV(NSTATV),
     1 DDSDDE(NTENS,NTENS),DDSDDT(NTENS),DRPLDE(NTENS),
     2 STRAN(NTENS),DSTRAN(NTENS),TIME(2),PREDEF(1),DPRED(1),
     3 PROPS(NPROPS),COORDS(3),DROT(3,3),DFGRD0(3,3),DFGRD1(3,3),
     4 JSTEP(4)

      REAL Tg,Tg0,Tg_inf,Lam,alpha,TT,TC1,TC2,Er,E0,E_INF,Poisr,Gr,
     1 Kr,Kf,ELf,Vf,PoisLTf,Kt,GLT,GTT,PoisLT,PoisTT,GLTf,GTTf,Del,nn

      Tg0=273
      Tg_inf=468
      Lam=0.4
      TC1=227
      TC2=261
      E0=3.447
      E_INF=3447
      ELf=73000
      Vf=0.6
      PoisLTf=0.22
      GLTf=ELf/(2*(1+PoisLTf))
      GTTf=GLTf
      nn=NOEL+4
      alpha=STATEV(nn)



      Tg=Tg0+Lam*alpha*(Tg_inf-Tg0)/(1-(1-Lam)*alpha)
      Temperature=STATEV(1)
      TT=Tg-Temperature
      if (TT.LE.TC1) then
          Er=E0
      else if (TT.LE.TC3) then
          Er=E0+(E_INF-E0)*(TT-TC2)/(TC3-TC2)
      else
          Er=E_INF
      end if
      STATEV(3)=Er

      Poisr=0.5-0.15*alpha
      Gr=Er/(2*(1+Poisr))
      Kf=ELf/(2*(1-PoisLTf-2*PoisLTf**2))
      Kr=Er/(2*(1-Poisr-2*Poisr**2))
      EL=ELf*Vf+Er*(1-Vf)+(4*(Poisr-PoisLTf**2)*kf*kr*Gr*(1-Vf)*Vf)/((Kf
     1 +Gr)*Kr+(Kf-Kr)*Gr*Vf)
      Kt=((Kf+Gr)*Kr+(Kf-Kr)*Gr*Vf)/((Kf+Gr)-(Kf-Kr)*Vf)
      GLT=Gr*((GLTf+Gr)+(GLTf-Gr)*Vf)/((GLTf+Gr)-(GLTf-Gr)*Vf)
      GTTf=ELf/(2*(1+PoisTTf))
      GTT=Gr*(Kr*(Gr+GTTf)+2*GTTf*Gr+Kr*(GTTf-Gr)*Vf)/(Kr*(Gr+GTTf)+
     1 2*GTTf*Gr-(Kr+2*Gr)*(GTTf-Gr)*Vf)
      PoisLT=PoisLTf*Vf+Poisr*(1-Vf)+(Poisr-PoisLTf)*(Kr-Kf)*Gr*(1-Vf)
```

```
     1 *Vf/((Kf+Gr)*Kr+(Kf-Kr)*Gr*Vf)
      PoisTT=(2*EL*Kt-EL*ET-4*(PoisLT**2)*Kt*ET)/(2*El*Kt)
      ET=1/((1/(4*Kt))+(1/(4*GTT))+(PoisLT**2)/EL)
C Building Jacobian Matrix
C Assumption of transversal isotropy
      Del=(1-2*PoisLT**2-PoisTT**2-2*PoisTT*PoisLT**2)/(ET*EL**2)
      DDSDDE(1,1)=(1-PoisLT**2)/(EL*ET*Del)
      DDSDDE(1,2)=(PoisTT+PoisLT**2)/(EL*ET*Del)
      DDSDDE(1,3)=(PoisLT+PoisLT*PoisTT)/(EL*ET*Del)
      DDSDDE(2,1)=DDSDDE(1,2)
      DDSDDE(2,2)=DDSDDE(1,1)
      DDSDDE(2,3)=(PoisLT+PoisLT*PoisTT)/(EL*ET*Del)
      DDSDDE(3,1)=(PoisLT+PoisLT*PoisTT)/(Del*ET**2)
      DDSDDE(3,2)=(PoisLT+PoisLT*PoisTT)/(Del*ET**2)
      DDSDDE(3,3)=(1-PoisTT**2)/(Del*ET**2)
      DDSDDE(4,4)=2*GLT
      DDSDDE(5,5)=2*GLT
      DDSDDE(6,6)=2*GTT
      do i=1,6
          do j=1,6
              STRESS(i)=STRESS(i)+DDSDDE(i,j)*DSTRAN(j)
          end do
      end do

      RETURN
      END
```

The UMAT subroutine is used to define the mechanical constitutive behaviour of the composite material by means of the mathematical model described in paragraph 4.5. In the first part the resin mechanical properties, functions of the degree of cure and temperature, are computed by means of the CHILE modified model and therefore it is possible to evaluate the lumped material properties. The Jacobian matrix DDSDDE is built and therefore the components of the stress vector are computed by means of the matrix product between the Jacobian matrix and the strain vector (DSTRAN).

```
      SUBROUTINE UEXPAN(EXPAN,DEXPANDT,TEMP,TIME,DTIME,PREDEF,
     1 DPRED,STATEV,CMNAME,NSTATV,NOEL)
C
      INCLUDE 'ABA_PARAM.INC'
C
      CHARACTER*80 CMNAME
C
      DIMENSION EXPAN(*),DEXPANDT(*),TEMP(2),TIME(2),PREDEF(*),
     1 DPRED(*),STATEV(NSTATV)
      Real Er,ELf,PoisLTf,Poisr,Vf,CTEL,CTET,CTELf,CTETf,CTEr,eps_thL,
     1 eps_thT,eps_chL,eps_chT,DV_sh

      Er=STATEV(3)
      ELf=73000
      Vf=0.6
      PoisLTf=0.22
      Poisr=0.5-0.15*STATEV(2)
      GLTf=ELf/(2*(1+PoisLTf))
      CTELf=5.04*10**(-6)
      CTETf=5.04*10**(-6)
      CTEr=50*10**(-6)
      DV_sh=1
```

```
C Thermic Strain
      CTEL=(CTELf*ELf*Vf+CTEr*Er*(1-Vf))/(ELf*Vf+Er*(1-Vf))
      CTET=(CTETf+PoisLTf*CTELf)*Vf+(CTEr+Poisr*CTEr)*(1-Vf)-(PoisLTf*Vf
     1 +Poisr*(1-Vf))*CTEL
      eps_thL=CTEL*(STATEV(1)-273)
      eps_thT=CTET*(STATEV(1)-273)
C Chemical strain
      eps_chL=(((1+STATEV(2)*DV_sh)**(1/3))-1)*Er*(1-Vf)/
     1 (ELf*Vf+Er*(1-Vf))
      eps_chT=(((1+STATEV(2)*DV_sh)**(1/3))-1)*(1-Poisr)*(1-Vf)-
     1 (PoisLTf*Vf+Poisr*(1-Vf))*eps_chL

      EXPAN(1)=eps_thT+eps_chT
      EXPAN(2)=EXPAN(1)
      EXPAN(3)=eps_thL+eps_chL
      DEXPANDT(1)=CTET
      DEXPANDT(2)=CTET
      DEXPANDT(3)=CTEL

      RETURN
      END
```

The UEXPAN is used to define incremental thermal and chemical strains. It follows the mathematical models described in particular in paragraph 4.5. The strains are used to update the array EXPAN. In this subroutine the value of the variation of thermal strains with respect to temperature must be defined and updated in DEXPANDT array.

```
      SUBROUTINE read_data(STATEV)

      CHARACTER*30 file1
      real, dimension (1444) :: STATEV
      real, dimension (1,1440) :: cure
C
      file1="C:\Users\Fausto\Desktop\Fausto\Cura.txt"
      open (unit = 1, file=file1)
      read (1,*) cure
      close (1)
      do i=1, num_el
          STATEV(i+4)=cure(1,i)
      end do

      RETURN
      END

      SUBROUTINE write_data(STATEV)

      real, dimension (1444) :: STATEV
      real,dimension (1,440) :: cure
      CHARACTER*30 file1

      do i=5, 1444
          cure(1,i-4)=STATEV(i)
      end do
      file1="C:\Users\Fausto\Desktop\Fausto\Cura.txt"
      open (unit = 1, file=file1, status='replace')
      write (1,*) cure
      close (1)

      RETURN
      END
```

The read_data and write_data subroutines are not within the default ABAQUS subroutines. They are called by the UEXTERNALDB subroutine. The first has the task to read the values of degree of cure from an external file and the second has the task to update the same files with the data computed during the current increment.

4.8 Finite difference model

In order to compare the results of the FEM model, a finite difference model of thermochemical phenomena has been implemented. The thermochemical problem (eq. (24) and (30)) has been first linearized by means of a first order truncation of the equations expansion in Taylor series. Particularly the non-linear term of Arrhenius relation has been linearized:

$$\exp\left(\frac{-E_a}{RT}\right)(1-\alpha)^n \sim \exp\left(\frac{-E_a}{RT_0}\right)(1-\alpha_0)^n\left[1+\frac{E_a}{RT_0^2}(T-T_0)-\frac{n}{1-\alpha_0}(\alpha-\alpha_0)\right]. \tag{55}$$

According to the finite difference theory the (1st and 2nd order) derivative terms in the node *j* have been transformed as follow:

$$\frac{\partial^2 T}{\partial x_i^2}=\frac{T_{j-1}-2T_j-T_{j+1}}{h_i^2}, \tag{56}$$

where x_i is one of the spatial coordinate and h_i is the spatial increment,

$$\frac{\partial T}{\partial z}=\frac{T_j-T_{j-1}}{h_z}, \tag{57}$$

where h_z is the increment in z direction,

$$\frac{\partial \alpha}{\partial z}=\frac{\alpha_j-\alpha_{j-1}}{h_z}. \tag{58}$$

With these approximations the continuous differential equations that describe the thermochemical behaviour of the system are transformed in many (discretized) coupled algebraic equations that can be solved with the support of a computer. This kind of problem require a set of boundary condition on a closed surface around the entire geometry. The boundary conditions are the same imposed for the FEM model. In this computation, as in the FEM model, one quarter of the system has been taken into account, therefore on the symmetry surfaces there should be symmetry conditions. The geometry of the problem impose a multigrid approach. Furthermore the presence of two different parts with different equations complicate the model. Referring to the nodes belong to the die an heat transfer static equation is implemented. On the nodes belonging to the external (lateral) surfaces of the mold the natural convective heat flow is shared, assuming the temperature of the environment of 293 K. On the composite part the model is composed of an heat transfer equation, with heat generation, related to the chemical process of cure. Since on the

composite parts there are two coupled equations (Heat transfer equation and degree of cure equation) and two different variable to define has been adopted a staggered grid. In Fig 32 the nodes disposition is shown: the temperature equations are wrote referring to each one of the red circles, while the cure equations are wrote referring to each one of the blue cross.
Because of the geometry of the system the problem is multigrid, therefore it is not always possible to use the equation (56). The correct form for the second spatial derivative in *x* and *y* direction is found each time taking into account the closer nodes temperatures. The accuracy chosen for the model is the first order in *z* direction and the second order in *x* and *y* direction.

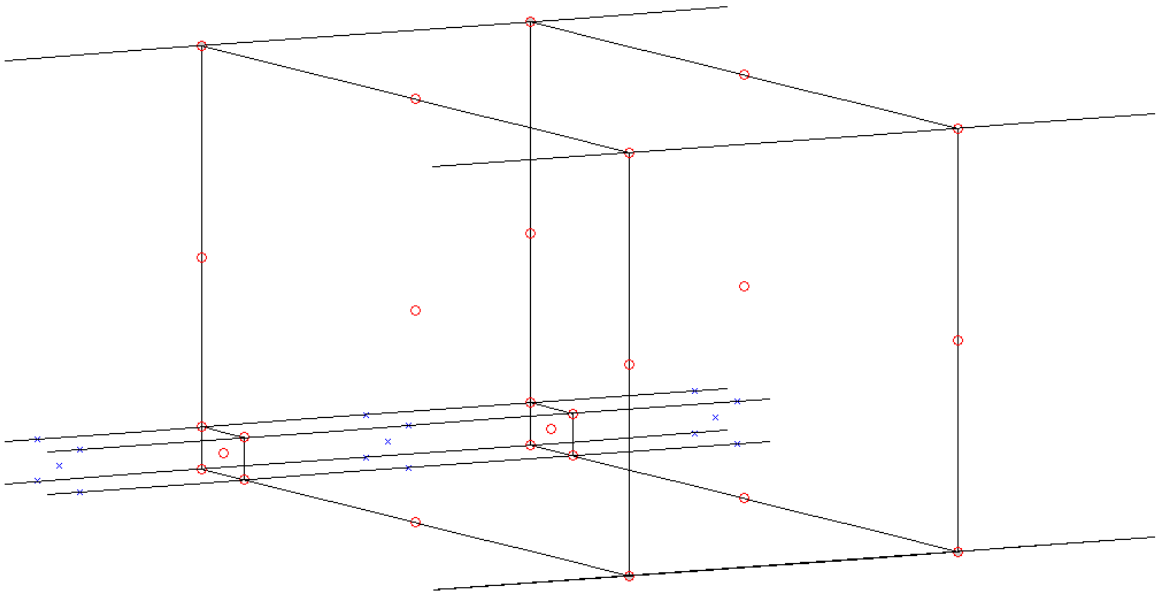

Fig 32: Nodes disposition

5. Discussion

In this dissertation it was documented the first part of a work in progress on the numerical modelling and simulation of pultrusion process on polymeric composite materials. A number of Fortran subroutines were developed, suited for application of the Finite Element Method within the commercial code ABAQUS. Those subroutines try to describe some of the many physical phenomena that take place during the pultrusion process, which were considered fundamental to build an adequate numerical tool for the analysis of the process, and the codes have been designed with the aim to be easily generalizable and modular.

The main milestones achieved have been the programming of the thermochemical model, essential for the description of all the other phenomena, and the programming of a mechanical model which takes account of polymerization of the resin, the thermal expansions and the chemical shrinkage.

The most imminent improvements which were taken into account in the later part of the work are related to the modelling of the interaction between the pultruded profile and the mold walls, in which the normal and tangential contact are related to the state of aggregation of the resin. This is due to the fact that in the sections in which the resin is still liquid occurs a viscous interaction, while on the walls of the mold it acts a hydrostatic pressure and, when it assumes the solid state of aggregation friction is considered. Another phenomenon that was taken into account was the springback of the composite material in the post-die region.

Subsequent developments of this work would have as their aim to get closer to the real process. This could be achieved by means of models of multilayer laminates, taking into account the presence (as it is often the case in industrial practice) of superficial layers that are reinforced by fibers fabrics mat structures, with completely different mechanical properties from the layers reinforced roving type. Another important improvement that can be made is the study of the processes that take place during the polymerization in the mesoscale or microscale. Doing so, many complex phenomena -such as impregnation, the trapping of air, the resin-fiber interaction- could be studied. A multiscale view would therefore lead to a deeper knowledge and consequently to a better ability to design both the system and the process, in part or *ex novo*, besides providing a suitable way to adjust operating parameters.

6. References

[1] P. Carlone, G.S. Palazzo, R. Pasquino, Pultrusion manufacturing process development by computational modelling and methods, Mathematical and Computer Modelling 44 (2006) 701-709.

[2] P. Carlone, G.S. Palazzo, R. Pasquino, Pultrusion manufacturing process development: Cure optimization by hybrid computational methods Computers and Mathematics with Applications 53 (2007) 1464–1471.

[3] P. Carlone, I. Baran, J. H. Hattel, G. S. Palazzo, Computational Approaches for Modeling the Multiphysics in Pultrusion Process (2013) 301875.

[4] T. A. Bogetti, J. W. Gillespie, Process-Induced Stress and Deformation in Thick-Section Thermoset Composite Laminates. J Compos Mater (1992) 26(5):626–60.

[5] F. Grasso, C. Calabretta, I materiali composite nei mezzi di trasporto. Università degli studi di Padova (2012).

[6] W. A. Stein, A summary of Classical Lamination Theory. (2010) Website: http://wstein.org/edu/2010/480b/projects/05-lamination_theory/ , date access: 17/07/2016

[7] G. Odian, Principles of Polymerization Fourth Edition, (2004) John Wiley & sons

[8] Website: https://it.wikipedia.org/ , date access: 17/07/2016

[9] Website: http://www.3ds.com/ , date access: 17/07/2016

[10] Website: http://www.technica.net/ , date access: 17/07/2016

[11] Website: http://www.libertypultrusions.com/, date access 17/07/2016

[12] P. Buccino, Progettazione di uno stampo per una linea di pultrusione in scala da laboratorio, (2013) Università degli studi di Salerno

[13] C. A. Felippa, Introduction to Finite Element Methods, (2004) University of Colorado

[14] Abaqus 6.14 User Subroutines Reference Manual (2015)